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Surface Treatment Agents for Protection of Shorelines from Oil Spills

Woodward-Clyde Consultants, San Francisco, CA

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SURFACE TREATMENT AGENTS FOR PROTECTION
OF SHORELINES FROM OIL SPILLS

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16. ABSTRACT

A literature review and laboratory tests were conducted to provide a basis for analyzing the results of previous tests on surface treatment agents, compare agent effectiveness, and recommend agents for preliminary field tests. The surface treatment agents evaluated during the preliminary tests were film-forming agents, dispersing agents, and a surface collecting agent. From the results of these tests, two film-forming agents, polyvinyl acetate and xanthan gum, a surface collecting agent, and a flowing film of water were recommended and tested during full-scale field tests at Sewaren Beach, New Jersey. The results of the full-scale field tests showed that polyvinyl acetate provided both beach and marsh test plots with the most effective long-term protection. The toxic effects of the various agents on the Eastern Blue Crab and cord grass (*Spartina foliosa*) were also evaluated.

This report was submitted in fulfillment of Grant No. R804639 awarded to the American Petroleum Institute under the sponsorship of the U.S. Environmental Protection Agency. The API awarded a contract to Woodward-Clyde Consultants, who, with their subcontractors, Texas Research Institute, Inc., and URS Research Company, completed the research in 1979. This report covers the period 1975-1979.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report describes the laboratory and field research that evaluated products and techniques for the protection and restoration of shorelines form oil spills. THe report will be of interest to those involved in oil spill prevention, control, and countermeasures.

Francis T. Mayo,
Director
Municipal Environmental Research Laboratory

ABSTRACT

Surface treatment agents for protecting shorelines from spills were evaluated by means of a literature review, laboratory tests, and field tests. Results of the literature review and laboratory tests were used as the basis for (1) analyzing the results of earlier tests on surface treatment agents for oil spills, (2) comparing effectiveness of surface treatment agents, and (3) recommending agents for preliminary field tests. Preliminary field tests of agent effectiveness, toxicity, and application techniqes were undertaken on slat-marsh sections and simulated beaches. The surface treatment agents tested during the preliminary field tests were film-forming agents (polyvinyl acetate, xanthum gum) and the surface collecting agents were recommended for and tested during the full-scale field tests at Sewaren Beach, New Jersey. In addition, a flowing film of water was tested for effectiveness as a surface treatment agent.

The results of the full-scale field tests showed that polyvinyl acetate provided both beach and marsh test plots with the most effective protection against the test oils (#6 fuel oil, #2 fuel oil, and Arabian crude oil) because it substantially decreased oil penetration, and it allowed surface oil to be easily removed by flushing. Xanthan gum was the least efective on the beach test plots of the three film-forming agents, but it did provide some beach substrate protection. On the marsh test plots, xanthan gum appeared to be the most effective short-term agent for protecting the vegetation and substrate from contamination by Arabian crude oil, but it was removed by flushing. The flowing film of water provided the best protection against beach surface contamination by oil, but it tended to erode channels in sand beaches, causing uneven coverage and allowing some oil penetration. The flowing film of water was not effective as a surface treatment agent for salt marshes because it could not provide a uniform film over the substrate and vegetation. The surface collecting agent was effective in confining oil under nonturbulent conditions. Turbulent conditions (caused by breaking waves impinging on the test area) caused the confined oil slick to break up.

Results of several studies are included as appendices to this report. They are: Prelimnary Agent evaluation Tests; Bioassay of Eastern Blue Crab with Surface Treatment Agents; Siedler Beach Surface Treatment Agents Tests; and Laboratory Investigation of Improved Materials for Shoreline Protection from Oil Spills.

This report was submitted in fulfillment of Grant No. R804639 by the American Petroleum Institute under the sponsorhsip of the U.S. Environmental Protection Agency. The API awarded a contract to Woodward-Clyde Consultants, who, with their subcontractors, Texas Research Institute, Inc., and URS Research Company, completed the research. The report covers the period July, 1975 to July, 1979, and work was completed by October, 1979.

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SECTION 1

INTRODUCTION

The state of the art for cleanup of oil-contaminated shorelines is well developed only for sandy beaches; cleanup of other oil-contaminated shoreline types requires extensive use of manual labor. The procedures for protecting shorelines from oil contamination are even less well developed and usually consist of deploying booms to direct oil away from a specific area. Wind, current, and surf action can, however, severely limit boom performance, allowing oil to escape and causing subsequent contamination of a shoreline.

In 1974, the American Petroleum Institute and the U.S. Environmental Protection Agency funded four laboratory projects to obtain information on materials that might be useful in protecting beaches and salt marshes from oil contamination. The results of these studies (1) identified eight natural and synthetic materials that, if applied to a beach or salt marsh, might offer the shoreline protection from oil contamination, and (2) recommended that the candidate agents that were identified be tested in the field under full-scale conditions.

The American Petroleum Institute obtained a research grant from the Environmental Protection Agency to continue this effort and awarded a contract to Woodward-Clyde Consultants and their subcontractors, Texas Research Institute, Inc., and URS Research Company. The purpose of the project was to evaluate, under field conditions, the effectiveness of the selected surface treatment agents in protecting beaches and salt marshes from oil spills and in assisting in the cleanup of shorelines previously contaminated by oil spill. Toxicity screening tests on cordgrass (Spartina foliosa) are discussed in Appendix B and on Eastern Blue Crab (Callinectus sapidus in Appendix C.

The scope of this project involved the following:

- Correlating data on the eight agents recommended by previous studies into a common baseline through literature reviews and laboratory testing.
- Conducting preliminary field tests with the agents and three types of oil (#2 fuel oil, Arabian crude oil, and #6 fuel oil) on marshgrass plots and simulated beaches to determine the most effective agents for full-scale field testing.

- Conducting full-scale field tests by applying the agents to actual beach and salt-marsh areas and contaminating the areas with three types of oil (#2 fuel oil, Arabian crude oil, and #6 fuel oil)

- Conducting preliminary toxicity tests of selected agents.

The surface treatment agents that were tested during the project are shown in Table 1.

REPORT ORGANIZATION

The remainder of this report presents specific details and information on the performance of the project. Section 2 presents conclusions of the full-scale field tests, and Section 3 states recommendations for agent use and additional research. Section 4 presents the results of the full-scale field test program at Sewaren, New Jersey. Specific data from the literature review, laboratory tests, and preliminary field tests are given in Appendices A and B. Appendix C gives the results of the eastern blue crab bioassay. Appendix D gives the results of the evaluation of surface treatment agents.

TABLE 1. SURFACE TREATMENT AGENTS EVALUATED DURING PROGRAM

Agents	Laboratory	Preliminary Field Tests Alameda	Full-Scale Field Tests Sewaren
Sodium silicate	x	x	
Sodium borate/sodium silicate mixture	x	x	
Citrus pectic	x	x	
Xanthan gum	x	x	x
Polyvinyl acetate	x	x	x
Flowing film of water	x		x
Surface collecting agent (Oil Herder)	x	x	x
Dispersant A (Correxit 7664)	x	x	
Dispersant B (BP 1100-X)		x	
Dispersant C (BP 1100 WD)		x	

SECTION 2

CONCLUSIONS

The full-scale field tests of surface treatment agents were undertaken as two tasks - one task for the beach testing and the other for the salt-marsh testing. Table 2 presents a ranking of the film-forming agents tested. Based on the results of the full-scale test program, the following conclusions are offered.

BEACHES

1. All three of the film-forming agents, polyvinyl acetate, xanthan gum, and a flowing-water film, provided some degree of protection from oil contamination of beaches. The polyvinyl acetate was the most successful of the agents tested, providing the best protection against oil penetration into the substrate.

2. The flowing-water film provided the best protection against beach surface contamination by oil. However, the tendency of flowing water to erode channels in sand and silt caused uneven water-film coverage on the beach and allowed some oil to penetrate the beach substrate.

3. Xanthan gum was the least effective of the three film-forming agents, but it did provide the beach substrate some protection from oil contamination.

4. Polyvinyl acetate proved to be the most durable film-forming agent; it remained on a test plot for at least eight tidal cycles. Polyvinyl acetate is also the agent that best facilitates oil removal from the test areas. Both #2 fuel oil and Arabian crude oil were almost entirely removed from the polyvinyl-acetate-coated surface by low-pressure water flushing. Only #6 fuel oil proved somewhat difficult to remove.

5. Of the three oils used in the test program (#2 fuel oil, Arabian crude oil, and #6 fuel oil), #2 fuel oil was the most difficult to protect the beach against; only polyvinyl acetate provided protection against #2 fuel oil penetration. Polyvinyl acetate, xanthan gum, and the flowing-water film were more successful in protecting the beach from Arabian crude oil and #6 fuel oil.

TABLE 2. RANKING* OF FILM-FORMING AGENTS EVALUATED DURING TEST PROGRAM

Agent	Film-Forming Agent Ranking								
	Sand Beach			Marsh					
	Oil Type			Oil Type					
	No. 6 Fuel Oil	No. 2 Fuel Oil	Arabian Crude Oil	No. 6 Fuel Oil		No. 2 Fuel Oil		Arabian Crude Oil	
				Short Term	Long Term	Short Term	Long Term	Short Term	Long Term
Polyvinyl acetate	1	1	1	2	1	1	1	2	1
Xanthan gum	3	3	3	1	2	2	3	1	2
Flowing water	2	2	2	3	3	3	2	3	3

* Agents are ranked in order of effectiveness in each test.

SALT MARSHES

1. Two of the surface treatment agents tested, polyvinyl acetate and xanthan gum, have definite potential for application in protecting salt marshes from oil contamination.

2. Polyvinyl acetate was particularly effective in protecting the salt marsh from contamination by #2 fuel oil and Arabian crude oil. Flushing of the oil from contaminated vegetation and marsh substrate was easier for PVA than with other agents or the control.

3. Xanthan gum appeared to be a slightly more effective short-term (i.e., hours) agent for protecting the marsh vegetation and substrate from contamination by Arabian crude oil. After a single flushing, however, the agent was largely removed from both plants and substrate.

4. The effectiveness of the continuous film of flowing water in marshes was limited. It was difficult to attain a uniform water flow that would protect both the vegetation and the substrate. Some protection was afforded the substrate, especially against the #2 fuel oil.

5. #6 fuel oil was extremely difficult to remove from both treated and untreated salt-marsh sections. Polyvinyl acetate and xanthan gum eased the flushing of the oil from the substrate in comparison with control sections. The xanthan gum, in particular, appeared to work better than polyvinyl acetate in facilitating #6 fuel oil removal from the substrate.

Surface Collecting Agents

Under the limiting conditions in which the beach and salt marsh surface collecting agent tests were conducted, the following conclusions were drawn.

The surface collecting agent was effective in confining oil under nonturbulent conditions. Turbulent conditions (caused by breaking waves impinging on the test area) caused the contained oil slick to break up. In the absence of the confining barriers used in the test, this effect may not have occurred. Oil washed into the marsh by turbulent conditions was easily removed from the plants by low-pressure water flushing.

General

Permit stipulations on the conduct of the full-scale field program, requiring that all test oils be contained within and removed from the test area, imposed restrictions on the "real-world" evaluation of the agents tested. Because of this restriction a great deal of effort was expended to ensure that oil was contained within the surrounding booms. In the case of the surface collecting agent test, this constriction interfered with the actual mechanism of the material being tested, that is, the surface collecting agent tended to drive oil away from the shoreline which was counteracted by

Toxicity testing of eight agents on Spartina foliosa (cordgrass) including relative comparisons of plant reaction (e.g., health) to various treatments made on the basis of qualitative observations and quantitative measurements of growth ratio were inconclusive.

Agent Toxicity

Toxicity testing of PVA and xanthan gum on juvenile callinectes (blue crabs) showed that:

1. The acute static bioassay successfully established 96-hour toxicity ranges for the two agents: PVA (0.45% to 3%) and xanthan gum (3% to 10%).
2. PVA (as applied at 100%) is seemingly more toxic to first-stage juvenile Callinectes than is xanthan gum (as applied at 1%).
3. The PVA at 0.45% concentration did not have any apparent physiological effect on the crabs during the 96-hour test period.
4. The xanthan gum at 3% concentration did not have any apparent physiological effect on the crabs during the 96-hour test period.
5. The 96-hour TLM for PVA was 0.95%.
6. The 96-hour TLM for xanthan gum was 5.5%.
7. The PVA seemed to act like a weak acid. The persistent low pH level in the 5% tank could have contributed to the toxicity of the agent. Additional tests on the chemical behavior of PVA in water are recommended.

SECTION 3

RECOMMENDATIONS

Based on the findings of this study, the following recommendations are offered:

1. Further research should be conducted to evaluate, under field conditions, other types of potential surface protection agents such as:

   * additional tests with surface collecting agents

   * dispersing agents

   * new film-forming agents, such as high-density, low-expansion foams or a polymeric high-expansion gel or foam

   * polyvinyl acetate with formulation adjectments to make it more readily degradable and to accelerate its drying time

2. All three film-forming agents should also be evaluated for effectiveness of protection against oil contamination on cobble and/or rock beaches.

3. Laboratory tests should be conducted with new agents to define their operation limits.

4. A prototype application system for beach and marsh areas should be designed and tests on an oil spill of opportunity using polyvinyl acetate as a surface treatment agent.

5. Additional testing in salt marshes is recommended to verify tests for agent toxicity. Experience gained in the preliminary work should permit development of refined and conclusive testing procedures.

6. Additional acute bioassay tests of PVA in the range of 0.45% to 3% and xantham gum in the range of 3% to 10% should be performed on first stage blue crab juveniles. Also, testing of post larval crabs, generally regarded to be more sensitive than first stage juveniles is recommended.

7. Organism toxicity of oil and oil plus agents should be determined on crabs through additional bioassay testing.

SECTION 4

FULL-SCALE FIELD TESTS

TEST SITE

The full-scale field tests were conducted at Sewaren Beach, located on the New Jersey side of the Arthur Kill, between the Public Service power plant on the north and the outlet of Smith Creek on the south (latitude 40 degrees 32 min. N, longitude 74 degrees 16 feet W) (Figure 1). Sewaren Beach is approximately 670 meters long and has been zoned a park site by the town of Woodbridge. The area is a former salt marsh that has been used as a disposal site for dredge spoils by the Corps of Engineers. The shoreline is composed primarily of gravel and coarse sand beaches interspersed with small patches of salt marsh on the southern end. The northern two-thirds of the intertidal beach area consists primarily of gravel; the southern third consists generally of gravel in the lower intertidal area and sand in the upper intertidal area, with scattered salt marsh in the foreshore area of the beach.

The land areas surrounding the Arthur Kill are heavily industrialized and densely populated. The Arthur Kill is an industrial waterway and is a heavily traveled component of the New York Harbor complex. Extensive dredging, landfilling, and bulkheading have eliminated much of the natural shoreline and wetlands.

Sewaren Beach is located along a section of the Arthur Kill that is subject to frequent oil spills. In 1973 the Arthur Kill from Linden to Perth Amboy was the scene of 147 separate oil spills, ranging in size from a few liters to 336,000 liters of oil. Twenty-nine of the 147 oil spills were greater than 378 liters and 11 were greater than 3,785 liters (USCG Pollution Incidence Reporting System). Because of the frequent oil spills in the area, the sand and gravel on Sewaren Beach contain residual weathered oil from past spills.

TEST OILS

Three types of oil were used to test the effectiveness of the surface treatment agents. The three oils present a wide spectrum of physical characteristics and are representative of the wide variety of crude and refined oils that could be accidentally released onto the water. Characteristics of the three test oils are given in Table 3.

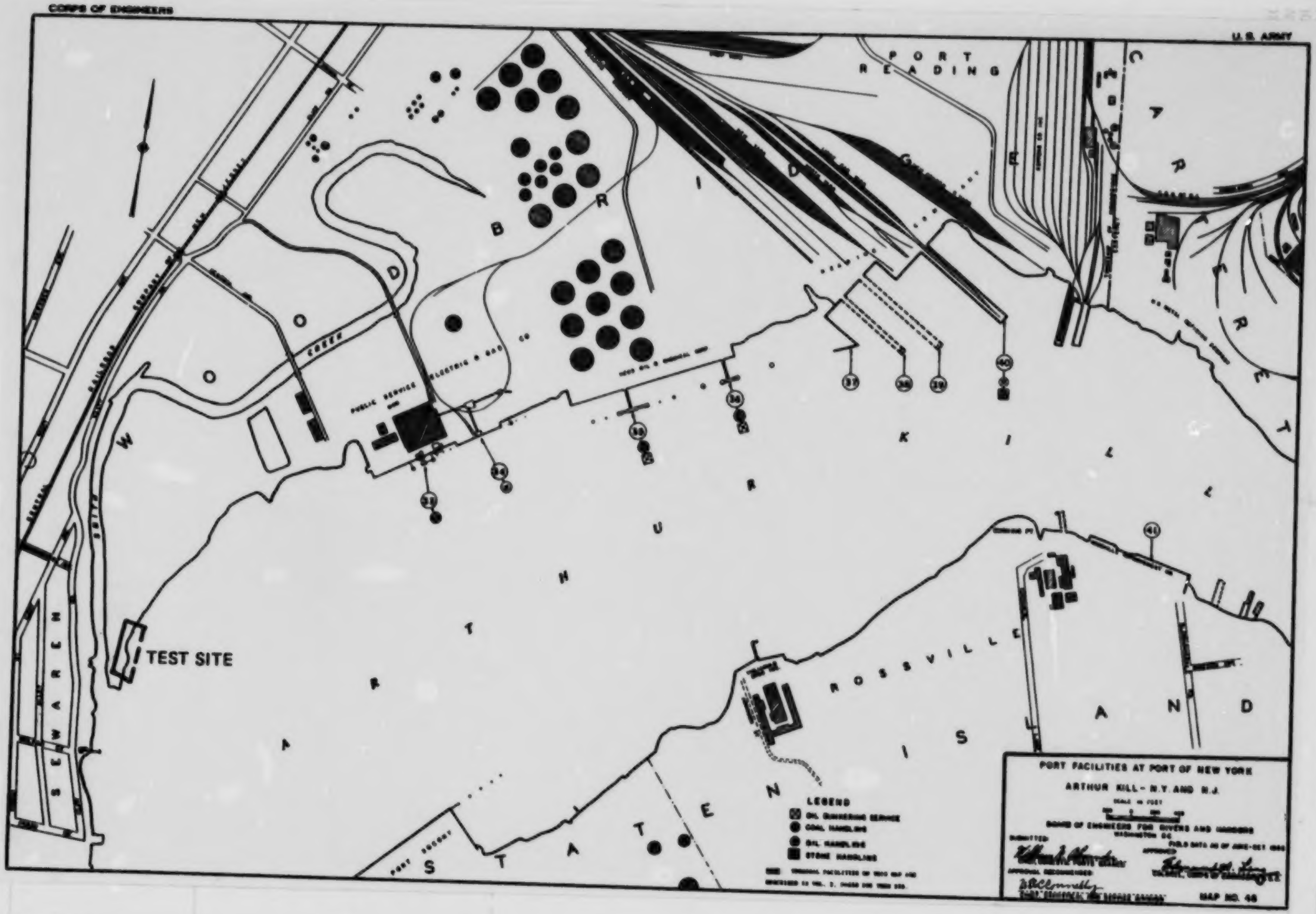
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Figure 1. Location of test site.

TABLE 3. CHARACTERISTICS OF TEST OILS

Characteristic	#2 Fuel Oil Min	#2 Fuel Oil Max	#6 Fuel Oil Min	#6 Fuel Oil Max	Arabian Crude
Gravity ($^{\circ}$API)	32.1	42.8	11.0	16.9	35
Viscosity					
Kinematic (100°F, CS)	2.35	3.0	--	--	8
Furol (122°, SFS)	--	--	101	250	--
Pour point ($^{\circ}$F)	--	0	--	35	-20
Sulfur content (wt, %)	--	0.35	--	2.73	2.5
Aromatics content (wt, %)	48	48	--	--	--
C_4 cut and lighter (wt, %)	--	--	--	--	2.88

AGENT EVALUATION PROCEDURES

The full-scale field tests were divided into two parts for the two tasks. The durability of the film-forming surface treatment agents was tested initially. Each candidate agent was applied to a marsh and beach test plot in the upper intertidal zone of the test site. Each test plot was observed and photographed during a tidal cycle and was sampled to determine the length of time each candidate agent remained on the shoreline surface as a viable surface treatment agent.

The second and more important part of the test program involved testing each candidate surface treatment agent for its ability to protect a shoreline surface when subjected to contamination from three different oils. This part of the program was further subdivided into two parts: film-forming agents and a surface collecting agent.

Film-Forming Agents

Test plots and control plots were laid out along a selected portion of the upper intertidal zone of the designated marsh and beach test zones. Each test plot was coated with a different candidate surface treatment agent, and the control areas were left in their natural state. Each beach test plot measured approximately 9.2 square meters. Each marsh test plot measured approximately 1.2 by 3 meters.

Booms were deployed in the water around the perimeter of the test zone.

Just prior to the tidal ebb, a specified volume of oil was released on the water inside the boomed test zone upwind from the test plots. The ebbing tidal action and prevailing wind deposited the oil on the surface of the shoreline test and control plots. After the tide had receded from the test and control plots, data were collected to assess the performance of each agent in protecting the shoreline from oil contamination. The conditions of the test plots were compared with the conditions of the oil-contaminated control plots. Following data collection, half of each beach test and control plot and the entire area of each marsh test and control plot on which oil remained were flushed with a low-pressure water system to determine the ease with which oil could be removed from an agent-coated surface. The other halves of the beach test and control plots were cleaned to determine if an agent-treated surface increases physical cleanup effectiveness.

Surface Collecting Agents

The surface collecting agent was tested separately because it would have affected the film-forming agent tests on adjacent plots. Booms were deployed in the water around the perimeter of the test zone, and the test oil (Arabian crude) was released prior to tidal ebb inside of the boomed zone. The surface collector was applied to the substrate of the beach and marsh test plots using an 18.9-liter hand-held garden sprayer, and it was also sprayed into the water ahead of the approaching oil slick. Data collection was conducted in a similar manner as for film-forming agents.

DATA COLLECTION

Photography was the major data-collection technique and was used primarily to record observations permanently. Photographs were taken of each test and control plot before and after each test to determine the degree of oil contamination. Depth of penetration of oil into the test plot was determined by cutting sections across a test plot, taking filter-paper blots at 7.6-cm and 15.2-cm depths, and examining the filter papers under ultraviolet light to determine the presence of oil by its characteristic fluorescence.

AGENT APPLICATION EQUIPMENT

Four types of equipment were used in applying the surface treatment agents during the full-scale field tests:

- hydraulic sprayer
- rotary pump
- water spray system
- garden sprayer

Film-Forming Agent Application

Because a hydraulic sprayer was successful in applying film-forming agents in the preliminary field tests, a hydraulic sprayer was used to apply xanthan gum and polyvinyl acetate for the first day of testing. Problems with the hydraulic sprayer occurred when the high pressure of the sprayer caused substrate disturbance of the beach test plots, and the nozzle of the sprayer clogged as the agents were being applied, causing lengthy delays. Therefore, the hydraulic spraying system was replaced by an alternative spraying system for the rest of the tests. The alternative spraying system consisted of a high-volume, positive-displacement, reversible rotary pump powered by a small (5.85-hp) diesel engine. The pumping rate was 64.4 liters/ minute at 1.75 to 2.1 kg per sq cm (25 to 30 psi) at 1000 rpm. A 5.1-cm suction hose and a 1.6-cm discharge hose with a hand-activated, adjustable piston-grip nozzle was used to apply agents. This combination provided a spray that gave an even coating to the shoreline substrate over a reasonable amount of time. There was no disturbance of beach substrate.

Water Film Application

The water-spray system was fabricated in the field; two 3-meter-long, 3.8-cm-diameter PVC pipe sections were joined by a 60-cm-long, 3.8-cm-diameter fire hose. A 5.1-cm trash pump (60-100 liters per minute) was used to pump salt water from a suction hose into the water-spray system. The 15-meter-long suction hose was suspended beyond the surf zone, below the water surface and above the bottom, to keep oil and bottom sediments from entering the water-spray system. Initially, fan spray heads from underground lawn sprinkling systems were inserted in the PVC pipe (30.5 cm apart). This provided a fine spray that created a continuous film of water over the substrate. These spray nozzles clogged with the algae and the suspended sediment entrained by the pump intake within several minutes. Holes measuring 1.2 cm in diameter were then drilled into the PVC pipe (30.5 cm apart). This allowed water to flow freely from the holes, forming a flowing-water film over the beach and marsh.

Surface Collector Application

An 18.9-liter low-pressure (1.75 kg per sq cm, 25 psi) hand-operated garden sprayer was used to apply the surface collecting agent.

TEST PROCEDURE

Table 4 gives the testing schedule and the environmental conditions at the test site at the times of agent application for the 4 days of testing. Figure 2 shows the test area, including the four test zones and the specific locations of the beach and marsh test plots.

Xanthan gum and polyvinyl acetate were applied (using the application techniques previously discussed) to the beach and marsh test plots between low tide and midtide and allowed to dry. The water-spray system was turned on at high tide and before the test oil was spilled. The surface collecting agent was applied to the beach and marsh test plots and to the water in front of the

TABLE 4. ENVIRONMENTAL CONDITIONS

Environmental Conditions at Agent Application	#6 Fuel Oil	#2 Fuel Oil	Arabian Crude Oil	
	May 21, 1977	May 23, 1977	May 24, 1977	May 25, 1977
Time of agent application to beach plots				
Xanthan gum	0830	0930	0950	
Polyvinyl acetate	0900	0955	1000	
Water	1100	1226	1315	
Surface collecting agent				1407
Air temperature	24-26°C	24-26°C	24-26°C	29-32°C
Wind speed	Less than 8 kph *	Less than 8 kph	8-16 kph	8 kph
Wind direction	SSE	SSE	SSE	SSE
Water salinity	25-30 ppt**	25-30 ppt	25-30 ppt	25-30 ppt
Height and time of high tide	1.4 m, 1100	1.3 m, 1226	1.4 m, 1315	1.4 m, 1407
Cloud cover	Hazy	10%	Hazy	Hazy
Beach type	Sand with some gravel	Sand and gravel	Sand and gravel	Sand and gravel
Area of beach plots	9.2 sq m	9.2 sq m	9.2 sq m	9.2 sq m

* kph = kilometers per hour.

** ppt = parts per thousand.

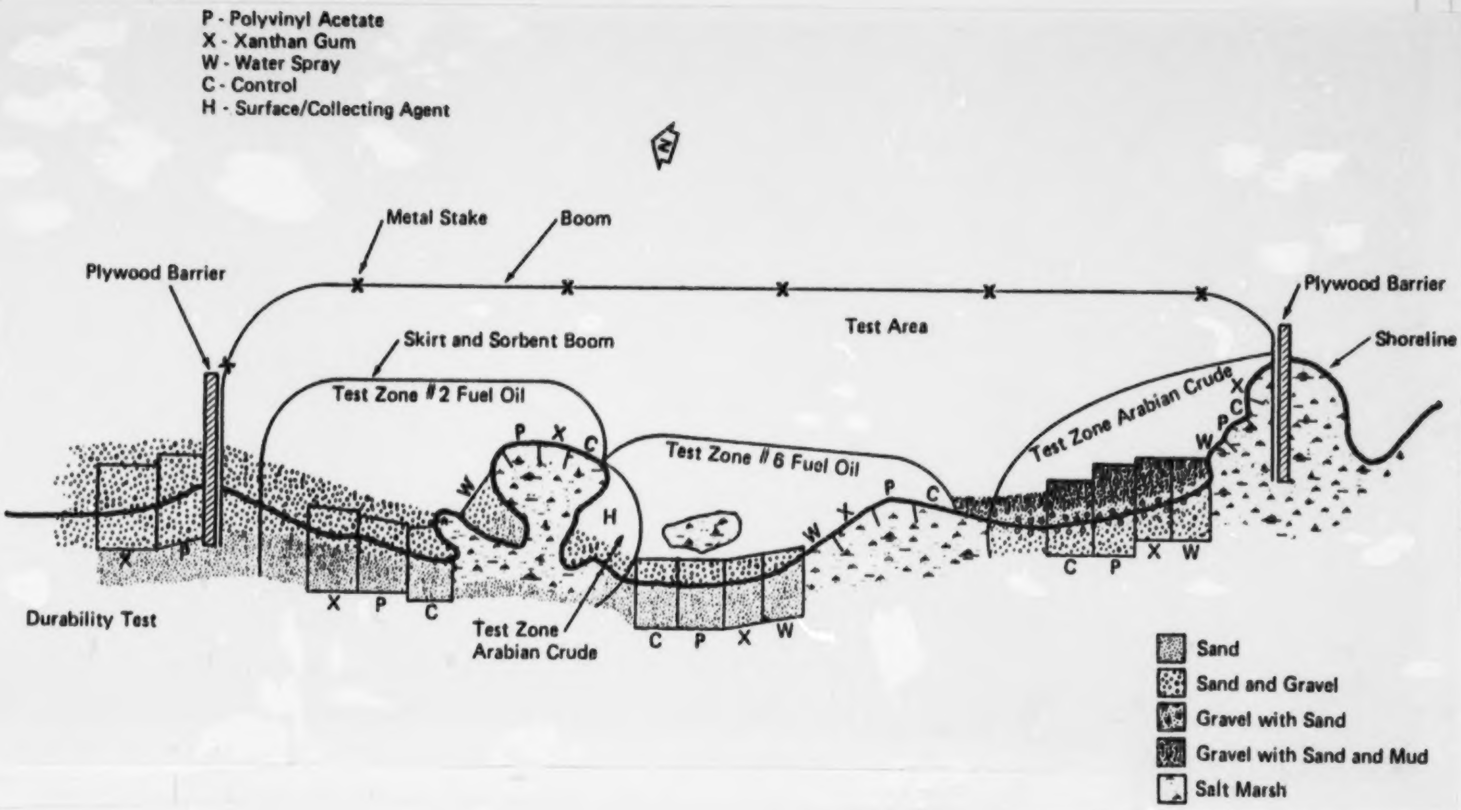
P - Polyvinyl Acetate
X - Xanthan Gum
W - Water Spray
C - Control
H - Surface/Collecting Agent
N
Metal Stake
Boom
Plywood Barrier
Plywood Barrier
Test Area
Shoreline
Skirt and Sorbent Boom
Test Zone #2 Fuel Oil
Test Zone #6 Fuel Oil
Test Zone Arabian Crude
Test Zone Arabian Crude
Durability Test
X P
X P C
P X C W
H
C P X W
W X P C
C P X W
W P C X
Sand
Sand and Gravel
Gravel with Sand
Gravel with Sand and Mud
Salt Marsh

Figure 2. Location of test plots in four test zones.

approaching oil slick after the test oil was spilled.

The test oils were spilled manually from an 18.9-liter bucket and were allowed to drift with the wind and current toward the test plots. Because the high tide did not fully cover some marsh test plots, oil was forced toward these plots by simulated wave action generated by a low-pressure water-spray system. This procedure was followed for each test oil and continued until a uniform coating of oil covered the vegetation and substrate. It was not possible to contaminate each plot entirely, but enough of the plots were covered to produce the desired results.

After completion of the tests, all test zones were cleaned manually with sorbents and low-pressure water flushing. The beach test plots were also cleaned mechanically by a front-end loader, which removed the contaminated beach material.

TEST RESULTS

Beach Tests

The major observations made and data collected during the full-scale tests at Sewaren, New Jersey, are given in Tables 5, 6, and 7. Included are data for each test, including the agent-application method, the volume of agent used, agent density (volume/sq meter) on each test plot, the time required to apply the agents, the time required for the film-forming agents to dry on each test plot, the percentage of oil coverage on each test plot after tidal deposition of the oil, and comments on the performance of the agents and the results of flushing oil from the agent surface. Drying times of the film-forming agents varied; pools of polyvinyl acetate and xanthan gum formed in depressions on the beach and took longer to dry because they were thicker than the rest of the film.

Flushing of oil from the film-forming agents was first attempted using sea water through a 3.8-cm fire hose attached to a 5.1-cm centrifugal trash pump. However, the pressure and volume of water was too great, and the fire-hose stream broke up the polyvinyl-acetate film and flushed oil into the sand substrate. A 1.6-cm hose with an adjustable pistol-grip nozzle attached to the same trash pump was then tried. It successfully flushed oil from the agent's surface without rupturing the film.

The effectiveness of each agent compared with a control in protecting the beach from oil contamination is given in Table 8. Following each test, the presence of oil on the surface of the test plots and the degree of oil penetration were determined by visual observation and by a sampling technique employing ultraviolet light. In this technique, which was developed by TRI, Whatman #1 filter paper was used to blot water from the beach sediments at the surface and at 7.6-cm and 15.2-cm depths. Each filter paper was then examined under ultraviolet light for the characteristic fluorescence of the test oil, and a semiquantitative determination was made of the amount of oil present. A subjective assessment of the degree to which oil covered each plot was made by visual observation. In the Arabian crude oil test, xanthan-gum, polyvinyl-acetate, and flowing-water-sheet test plots were significantly less

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TABLE 5. SURFACE TREATMENT AGENT BEACH FIELD TEST: #6 FUEL OIL (volume spilled: 114 liters)

	Agent Tested			
	Polyvinyl Acetate	Xanthan Gum	Water Spray	Control
Application method and spray pressure	Hydraulic sprayer at 42 kg/sq cm (600 psi); also poured agent onto test plot*	Hydraulic sprayer at 42 kg/sq cm (600 psi); also poured agent onto test plot*	Continuous water flow at 60-100 liters/min	--
Volume of agent used	5.7 liters sprayed; 3.8 liters poured	15 liters sprayed; 19 liters poured	--	--
Agent application density	1 liter/sq meter	3.7 liters/sq meter	3-5 liters/sq meter	--
Time required to spray agent (min or sec)	10-15 min	20 min	--	--
Agent drying time	1.5-2 hr	1 hr	--	--
Oil coverage on test plot after test	100% of area covered by tide	40-50% of area covered by tide	20-30% of area covered by tide	100% of area covered by tide
Comments	Agent film in lower intertidal area of test plot was dissolved by tide before it had properly dried	Agent film in lower intertidal area of test plot was dissolved by tide before it had properly dried	Flowing water eroded channels in sandy sections of test plot. Oil did not adhere or penetrate in areas where water flowed but did contaminate areas where water film did not cover due to erosion channels	--
Results of surface flushing	Flushing with a fire hose ruptured polyvinyl acetate film, causing oil to penetrate beach substrate. Flushing with garden hose removed most of the oil from polyvinyl acetate film. Film remained stained, however.	Flushing removed only some oil from surface	--	Oil not removed by flushing

* The volume of agents sprayed by the hydraulic spraying system was too small to use on a large scale. Therefore, a different spraying system was used for other tests.

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TABLE 6. SURFACE TREATMENT AGENT BEACH FIELD TEST: #2 FUEL OIL
(volume spilled: 190 liters)

	Agent Tested			
	Polyvinyl Acetate	Xanthan Gum	Water Spray	Control
Application method and spray pressure	Viking gear pump and 1.6-cm hose with garden spray nozzle at 1.4-2.1 kg/sq cm (20-30 psi)	Viking gear pump and 1.6-cm hose with garden spray nozzle at 1.4-2.1 kg/sq cm (20-30 psi)	Continuous water flow, 60-100 liters/min	--
Volume of agent used	23-30 liters	57 liters	--	--
Agent application density	2.5-3.3 liters/sq meter	6.2 liters/sq meter	3-5 liters/sq meter	--
Time required to spray agent (min or sec)	1 min	50 sec	--	--
Agent drying time	1-1.5 hrs	45 min	--	--
Oil coverage on test plot after test	100% of area covered by tide	100% of area covered by tide	100% of area covered by tide	100% of area covered by tide
Comments	--	--	Where water was flowing on test plot there was no oil contamination (sheen in other areas); channel erosion a problem	--
Results of surface flushing	Most of oil flushed from film by garden hose spray	Very little oil removed with flushing by garden hose spray	--	Oil not removed by flushing

TABLE 7. SURFACE TREATMENT AGENT BEACH FIELD TEST: ARABIAN CRUDE OIL
(volume spilled: 95 liters)*

	Agent Tested				
	Polyvinyl Acetate	Xanthan Gum	Water Spray	Control	Surface Collector
Application method and spray pressure	Gear pump and 1.6-cm hose with garden spray nozzle at 1.4-2.1 kg/sq cm (20-30 psi)	Gear pump and 1.6-cm hose with garden spray nozzle at 1.4-2.1 kg/sq cm (20-30 psi)	Continuous water flow at 60-100 liters/min	--	Sprayed onto shoreline and into water ahead of approaching oil slick
Volume of agent used	15 liters	57 liters	--	--	1 liter
Agent application density	1.6 liters/sq meter	6 liters/sq meter	3-5 liters/sq meter	--	--
Time required to spray agent (min or sec)	50 sec	50 sec	--	--	5 min
Agent drying time	1-2 hr	1-1.5 hr	--	--	--
Oil coverage on test plot after test	100% of area covered by tide	100% of area covered by tide	Less than 10% of area covered by tide	100% of area covered by tide	100% of area covered by tide
Comments	Polyvinyl acetate had less surface oil contamination than xanthan gum but more than flowing water film	More oil on xanthan gum test plot than polyvinyl acetate and flowing water film	Flowing water film test plot appeared to have least surface contamination; more gravels in this test plot, so erosion was less and therefore oil contamination was less	--	--
Results of surface flushing	Successfully removed almost all oil from	Flushing removed some oil from surface	--	Flushing did not remove any oil	--

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* The surface collector was tested separately using 38 liters of Arabian crude oil.

TABLE 8. BEACH SURFACE TREATMENT AGENT COMPARISON

			Presence of Oil (Comparison to Control)					
			Ultraviolet Light Samples			Visual Observation (Surface Only)		
Oil	Agent	Sample	Better	Same	Worse	Better	Same	Worse
#6 Fuel	Polyvinyl acetate	Surface		x			x	
#6 Fuel	Xanthan gum	Surface		x		x		
#6 Fuel	Water	Surface		x		x		
#6 Fuel	Polyvinyl acetate	7.6-cm cross-section	x					
#6 Fuel	Xanthan gum	7.6-cm cross-section		x				
#6 Fuel	Water	7.6-cm cross-section	x					
#6 Fuel	Polyvinyl acetate	15.2-cm deep	x					
#6 Fuel	Xanthan gum	15.2-cm deep	x					
#6 Fuel	Water	15.2-cm deep	x					
#2 Fuel	Polyvinyl acetate	Surface		x			x	
#2 Fuel	Xanthan gum	Surface			x		x	
#2 Fuel	Water	Surface	x			x		
#2 Fuel	Polyvinyl acetate	7.6-cm cross-section	x					
#2 Fuel	Xanthan gum	7.6-cm cross-section		x				
#2 Fuel	Water	7.6-cm cross-section		x				
#2 Fuel	Polyvinyl acetate	15.2-cm deep	x					
#2 Fuel	Xanthan gum	15.2-cm deep			x			
#2 Fuel	Water	15.2-cm deep			x			
Arabian crude	Polyvinyl acetate	Surface		x		x		
Arabian crude	Xanthan gum	Surface			x	x		
Arabian crude	Water	Surface		x		x		
Arabian crude	Polyvinyl acetate	7.6-cm cross-section	x					
Arabian crude	Xanthan gum	7.6-cm cross-section	x					
Arabian crude	Water	7.6-cm cross-section	x					
Arabian crude	Polyvinyl acetate	15.2-cm penetration	x					
Arabian crude	Xanthan gum	15.2-cm penetration	x					
Arabian crude	Water	15.2-cm penetration			x			
Arabian crude	Surface Collecting Agent	Surface		x			x	
		7.6-cm cross-section		x				
		15.2-cm penetration			x			

contaminated by oil than the control plot. However, surface sampling by filter-paper blotting of these test plots indicated that the presence of hydrocarbons was equivalent to or greater than that of the control. This is because the ultraviolet-light detection technique does not discriminate between high and low levels.

The beach-test results indicated that polyvinyl acetate was superior in preventing oil from penetrating the beach sediment. Although oil contamination of the polyvinyl-acetate surface was greater in some cases than for other agents, it proved to be the agent that could be cleaned most easily by flushing with a low-pressure water system. The most difficult oil to protect the beach against was #2 fuel oil; only polyvinyl acetate provided protection against #2 fuel oil penetration.

The surface collecting agent initially was very successful in preventing Arabian crude oil from reaching the beach test plot. The surface collecting agent formed a barrier in the water in front of the test plot and drove the advancing oil slick back against the containment boom that surrounded the test zone. A water stream from a fire hose was used to hold the oil away from the containment boom. After approximately 20 minutes, breaking waves impinged on the test zone, causing the contained oil slick and chemical barrier to break up into numerous small oil slicks, some of which came ashore contaminating the test plots. Without the containment barrier, the surface collecting agent may have held the slick offshore effectively.

Beach tests of the durability of the film-forming agents, polyvinyl acetate and xanthan gum, were also conducted during the full-scale field test program. Xanthan gum and polyvinyl acetate were each applied to a 10-square-meter test plot in the upper intertidal zone of the test site at application densities of 6 liters per sq meter for xanthan gum and 3 liters per sq meter for polyvinyl acetate. The xanthan-gum film was intact (i.e., maintained film integrity) after one tidal cycle, but had essentially disappeared except for an occasional patch after the second tidal cycle. The polyvinyl acetate proved much more durable and was still intact at the conclusion of the test program four days and eight tidal cycles later.

DISCUSSION

Protection Effectiveness

The effectiveness of surface treatment agents in protecting beach and salt marsh areas from oil contamination varied with the type of oil spilled and the type of beach.

Polyvinyl Acetate—

Of the four agents evaluated, polyvinyl acetate provided the most effective protection from the three test oils. The use of polyvinyl acetate substantially decreased oil penetration into the beach substrate as compared with the control, although surface contamination was similar to the control in two of the three tests. Polyvinyl acetate dried to a firm, semi-pliant film that could be peeled almost intact from the beach surface. The agent can be applied full strength (without dilution or mixing) at a rate of approximately

10 sq meters per minute with a rotary pump system. However, before it is effective as a film-forming agent, polyvinyl acetate requires time to dry. If it is still liquid or semi-liquid when it contacts water, it will dissolve into the water column. Once dried, the polyvinyl acetate film is very durable against tidal action and small waves. However, this is only true as long as waves do not impinge on the beach above the upper limit of the polyvinyl-acetate film, where the wave backwash can get under the film and destroy its integrity.

Xanthan Gum—

Xanthan gum was less effective than either polyvinyl acetate or the flowing-water film in protecting the beach test plots from oil penetration, although in the #6 fuel oil test there was less surface oil contamination of the xanthan-gum-coated test plot than of the polyvinyl-acetate-coated plot. Xanthan gum was applied in a 1% water solution (by weight) with the rotary pump system, at a rate of approximately 10 sq meters per minute (similar to polyvinyl acetate). It dried somewhat more rapidly than polyvinyl acetate to a soft, jellylike film. Like polyvinyl acetate, if water contacts xanthan gum before it dries, it will dissolve into the water column. A xanthan-gum protective film will last for approximately one to two tidal cycles before its integrity is lost. Xanthan gum is commercially sold as a dry powder (used in drilling mud) and does not dissolve easily, requiring mechanical stirring to effect a solution. The xanthan-gum powder must be sifted as it is added slowly to the vortex of the water or it forms clumps. It required approximately 10 minutes to mix 113.6 liters of 1% xanthan gum solution.

Flowing-Water Film—

A flowing film of water was less effective than polyvinyl acetate, but somewhat more effective than xanthan gum in protecting beach test plots from oil contamination. Of all the agents tested, the water film provided the best protection from surface oil contamination, but it allowed more oil penetration into the beach substrate than polyvinyl acetate.

The flowing film of water, applied at a rate of 3 to 5 liters per sq meter, tended to cause channel-type erosion on sandy sections of the test plots. This erosion resulted in an uneven distribution of the water film (i.e., water flowed in the channels in the sand). The high spots between the channels were not covered by the water film, and they became contaminated by oil. If channelization had not occurred (as would be the case on gravel, cobble, or rock beaches), the flowing-water film would have been an even more effective protection agent. A recurring problem with the flowing-water system was clogging of the water distribution pipes and outlet holes by filamentous algae and sediment picked up by the water pump suction line.

Surface Collecting Agent

The surface collecting agent provided an effective chemical barrier that prevented oil from reaching the shoreline until wave action disrupted the contained oil slick, allowing some oil to be carried ashore. The inner oil boom surrounding the test area was only 5 to 8 meters from the high tide lines. This close boundary may have interfered with the evaluation of the surface collecting agent. Within seconds after applying the surface

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collector, the oil slick contracted into a narrow band against the inner boom.

A water stream from a fire hose was used throughout the test to hold the oil slick away from the boom. However, the contained oil slick was not broken up until breaking waves passed through the test area. Once the slick was disrupted into small oil slicks or spots, the water stream and prevailing winds helped carry some of the oil ashore.

Oil-Contamination Sampling

The ultraviolet-light detection technique used to determine the penetration of the agent by a test oil is extremely sensitive to the aromatic hydrocarbons present in oils, especially light fractions. As performed, a blot sample is taken from the beach on a Whatman #1, 9-cm-diameter filter paper. This filter paper absorbs aromatics if present in even a small quantity. Subsequent examination of the paper under short-wave (2500 Å) ultraviolet light will show a characteristic fluorescence only in the area of test paper contacted by the oil.

This test is semiquantitative in nature. It will not accurately determine quantitative amounts of oil penetrating a beach, but will show the degree of presence or absence of the oil. Also, the source of oils detected is not specific to those spilled. Any contamination present in the beach strata from earlier spills may be detected. Test samples taken from the Sewaren Beach test site prior to agent testing in fact showed detectable levels of oil.

The following conclusions can be mde from the results of the blot tests:

- All beach samples examined showed the presence of oil under the surface prior to the test series. Surface examination showed no oil.
- Comparison of visually observable surface contamination to blot-test penetration samples may not correlate because of blot-test sensitivity and the colorless nature of light components of the oils.
- General trends of effectiveness can be determined from the combined results of visual and ultraviolet observations.

Effectiveness of Surface Oil Removal

The degree to which the xanthan-gum and polyvinyl-acetate-coated beach test plots could be cleaned of surface oil contamination was evaluated for the three test oils. This evaluation was undertaken to determine if the agent-treated surface affected the effectiveness of cleanup operations. Low-pressure water flushing was employed to clean oil from the agent's surface. In all three cases, the polyvinyl-acetate film was cleaned more effectively than the xanthan-gum film. The fuel oil that was the most difficult to flush was #6 fuel oil; very little was removed from the xanthan-gum surface and an oil stain remained on the polyvinyl-acetate film after flushing.

A brief test was performed on the polyvinyl-acetate and xanthan-gum test plots to determine if the use of these film-forming agents would make cleanup of oil-contaminated beaches by heavy equipment easier. A small rubber-tired front-end loader, using its powered bucket as a scraper, dragged the bucket across each beach test plot. The xanthan-gum film broke up and did not enhance removal. The polyvinyl-acetate film was peeled from the beach surface, making surface cleanup easier.

Salt Marsh Tests

Each test plot was exposed to approximately one-eighth of the total volume of oil spilled. There were four marsh test plots tested with each oil and, depending on the total volume of oil spilled, each plot was exposed to 12 to 15 liters. The results of the marsh tests are shown in Tables 9, 10, and 11.

All of these test results are based on observations made during and shortly following the application of agents and oils. In the tables, short-term effectiveness refers to observations made during and immediately following each test. Long-term effectiveness is based on a composite of observations made each day for 3 days after a particular test. Agents are ranked according to their relative effectiveness. For the Arabian crude oil test, the ranking ranged from 1 to 3 and compared the agents with each other. An additional evaluation was made in order to determine whether the agent-treated test plots produced results better than, worse than, or the same as the control test plot.

#6 Fuel Oil—

Four 1.2- by 3-meter marsh plots of Spartina alterniflora were marked off for testing with #6 fuel oil. Approximately 14 liters of oil contaminated each marsh plot. The test plots consisted of a control plot, a plot treated with approximately 10 liters of polyvinyl acetate, a plot treated with 30 to 35 liters of xanthan gum, and a plot that used a continuous water film as the surface treatment agent. Because of initial problems with the application system, the polyvinyl acetate and xanthan gum were applied by both spraying and pouring the agents onto the marsh plot. Table 9 summarizes the results of this test.

Xanthan gum appeared to provide the most effective protection for the short term (immediately following contamination). Oil was easily removed from the substrate by flushing with low-pressure water. This is in contrast to a fair to good flushing result in the polyvinyl-acetate-treated plots and fair removal from the control plot. Extensive adherence of the oil to the vegetation was observed with all three agents and the control, with little distinguishing differences. The xanthan gum was essentially 100% removed by low-pressure flushing on both the vegetation and the substrate. Observations of the test plot the day after the test revealed little or no agent present.

The water-spray system did not provide complete protection because obtaining a uniform flow over the substrate and the vegetation was difficult. The primary effectiveness of the water spray was on the substrate, but as noted, it was limited. Another problem with the water-spray system occurred

TABLE 9. SURFACE TREATMENT AGENT MARSH FIELD TEST: #6 FUEL OIL
(volume spilled: 114 liters)

Agent	Soil Penetration	Ease of Oil Removal by Flushing		Degree of Agent Removal by Flushing		Natural Deterioration of Agent (After Flushing)		Relative Effectiveness		Comparison to Control
		Substrate	Vegetation	Substrate	Vegetation	Substrate	Vegetation	Short Term	Long Term	
Polyvinyl acetate	None observed	Fair to good removal; required extensive flushing	Poor removal; extensive oil adherence; approximately 50-75% remained	Integrity of film disrupted; approximately 50-75% remained	Some film disruption; most still remained	Slow; approximately 50% still visible after 3 days	Very slow; none observed during test; peeling off in 1-2 days	2	1	Better than control
Xanthan gum	None observed	Good removal obtained	Poor removal; extensive oil adherence	Most or all of agent removed after flushing	Most of agent removed after flushing	Rapid; agent not flushed rapidly removed by waves and tides	Rapid removal of agent by waves and tides	1	2	Better than control
Control	None observed	Fair removal; patches difficult to flush	Poor removal; extensive adherence	N.A.	N.A.	N.A.	N.A.	-	-	--

Agent	Duration of Protection (Nonturbulent)	Response to Waves (Turbulent)	Comments	Short Term	Long Term	Comparison to Control
Water spray	Unlimited	Splashing has a tendency to deposit oil behind spray system	Protection was not complete; difficult to obtain a uniform flow; primary effectiveness on substrate	3	3	No difference

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TABLE 10. SURFACE TREATMENT AGENT MARSH FIELD TEST: ARABIAN CRUDE OIL (volume spilled: 95 liters)

Agent	Soil Penetration	Ease of Oil Removal by Flushing		Degree of Agent Removal by Flushing		Natural Deterioration of Agent (After Flushing)		Relative Effectiveness		Comparison to Control
		Substrate	Vegetation	Substrate	Vegetation	Substrate	Vegetation	Short Term	Long Term	
Polyvinyl acetate	None to limited; lack of penetration may reflect completeness	Fair to good removal; dependent upon surface irregularities	Nearly complete	Integrity of film disrupted; 50-75% remained	Some film disruption; most still remained	Slow; approximately 50% of agent still visible after 3 days	Slow; agent began to peel off in 1-2 days	2	1	Better than control
Xanthan gum	None to limited; lack of penetration may reflect film completeness	Fair to good removal; dependent upon surface irregularities; slightly better than polyvinyl acetate	Nearly complete	Most of agent removed by flushing	Most or all of agent removed rapidly by waves and tides	Rapid; agent not flushed removed rapidly by waves and tides	Rapid; agent removal by tide and waves not quite as rapid as substrate	1	2	Better than control
Control	Yes; particularly in upper 2-4 cm	Only fair removal; only on surface	Fair to good	N.A.	N.A.	N.A.	N.A.	-	-	--
	Duration of Protection (Nonturbulent)		Response to Waves (Turbulent)		Comments					
Water spray	Unlimited		Splashing had a tendency to deposit oil behind spray		Protection was not complete; difficult to obtain a uniform flow; primary effectiveness on substrate			3	3	No difference
Surface collecting agent	Effective		Breaking waves disrupted the oil slick into nuclear slicks which did not recombine		Initially effective when calm, repetitive applications were unsuccessful; possible test interferences			Not rated		

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TABLE 11. SURFACE TREATMENT AGENT MARSH FIELD TEST: #2 FUEL OIL
(volume spilled: 190 liters)*

Agent	Soil Penetration	Ease of Oil Removal by Flushing: Substrate	Ease of Oil Removal by Flushing: Vegetation	Degree of Agent Removal by Flushing: Substrate	Degree of Agent Removal by Flushing: Vegetation	Natural Deterioration of Agent (After Flushing): Substrate	Natural Deterioration of Agent (After Flushing): Vegetation	Relative Effectiveness: Short Term	Relative Effectiveness: Long Term	Comparison to Control
Polyvinyl acetate	None to limited; film very complete, limited penetration	Good; most oil easily flushed out	Good; most oil easily flushed off	Integrity of film disrupted; 50-75% remained	Integrity of film disrupted; 50-75% remained	Slow; approximately 50% of agent remained after 3 days	Slow; agent began to peel off in 1-2 days	1	1	Better than control
Xanthan gum	None to limited; but oil may penetrate during flushing	Fair; oil may penetrate during flushing	Good; shiny appearance reduced or disappears	Most of agent removed	Most or all of agent removed by flushing	Rapid; agent not flushed rapidly removed by tides and waves	Rapid; agent not flushed rapidly removed by tides and waves	2	3	Better than control
Control	Yes	Poor; only oil on surface removed	Fair to good; shiny leaves indicate oil still present after flushing	N.A.	N.A.	N.A.	N.A.	-	-	--
	Duration of Protection (Nonturbulent)		Response to Waves (Turbulent)		Comments					
Water spray	Unlimited		Splashing has a tendency to deposit oil behind spray		Protection was not complete; difficult to obtain a uniform flow; primary effectiveness on substrate; works better than on #6 fuel oil, especially to limit substrate penetration			3	2	Better than control

* Presence of thin films of oil was extremely difficult to detect visually on both plants and substrate.

during periods when large waves were generated by passing tugboats. The waves had a tendency to transport and deposit the oil behind the flowing film, partially negating the effect of the film.

Flushing with low-pressure salt water caused disruption of film integrity on the substrate of the polyvinyl-acetate plot; approximately 50% to 75% of the film remained. Most of the film remained on the vegetation after flushing, and the cordgrass retained its brittle texture. After one to two days natural deterioration by waves, wind, and tide began to cause peeling. Approximately 50% of the polyvinyl acetate was still visible on the substrate after three days, although it was slowly hydrolyzing.

No substrate penetration by #6 fuel oil was observed for either treated or control marsh plots. This was due primarily to the high viscosity of the oil and the low porosity of the substrate.

Each film-forming agent was ranked in terms of its effectiveness in protecting the salt marsh from contamination by #6 fuel oil. The xanthan gum was ranked first because of the slightly better results obtained when flushing the substrate. Polyvinyl acetate was ranked ahead of the flowing film of water because of the problems with the oil depositing behind the spray system during periods of high waves.

In comparison with the control plot, use of the polyvinyl acetate and xanthan gum proved more effective than no protection at all. In particular, removal of the oil from the substrate was enhanced by using the two agents. The water film was also slightly better because it prevented the oil from adhering to areas where the water was flowing. Because of the nonuniform flow on substrate and vegetation and problems with the waves depositing oil behind the spray, the water-spray plot was considered little different from the control plot.

Arabian Crude Oil—

Five 1.2- by 3-meter marsh plots of Spartina were used to conduct the tests with Arabian crude oil. In addition to the polyvinyl-acetate, xanthan-gum, control, and water-spray plots, another plot was tested using the surface collecting agent. Table 10 summarizes the results of the Arabian crude oil test.

Each marsh plot was exposed to approximately 12 liters of oil. The polyvinyl acetate and the xanthan gum were applied with a rotary pump. More of each agent (approximately 15 liters of polyvinyl acetate and 57 liters of xanthan gum) was used in this test. The water-spray system was the same system used in the #6 fuel tests.

Xanthan gum and polyvinyl acetate provided the most effective marsh protection of all the agents tested, but xanthan gum appeared to work slightly better than the polyvinyl acetate in enhancing flushing of the oil from the substrate (similar to the #6 fuel oil tests). Both agents were successful in providing nearly complete protection for the vegetation from oil after flushing; removal of oil from the substrate and vegetation was only fair to good on the control plot. This indicates the effectiveness of the polyvinyl acetate and xanthan gum as surface treatment agents.

The water-spray system did not provide complete protection because of the lack of uniform water flow over the substrate and the vegetation. Waves generated by passing tugboats transported and deposited oil behind the spray system. Water spray was most effective on the substrate in which the water flow prevented penetration of the substrate and adherence to the vegetation.

Flushing with low-pressure water spray caused disruption of the polyvinyl-acetate film on both the substrate and vegetation, especially on the vegetation. The brittle texture of the plants indicated that most of the film still remained on the vegetation. After three days, approximately 50% of the polyvinyl acetate remained on the substrate, indicating the slow natural deterioration of the agent. The leaves showed signs of the polyvinyl acetate peeling off after one to two days.

Xanthan gum was easily flushed from both the marsh substrate and the vegetation immediately following contamination by the oil. The residual xanthan gum disappeared rapidly after one tidal cycle. This shows that xanthan gum does not provide any long-lasting protection.

Polyvinyl acetate and xanthan gum appeared to prevent significant oil penetration into the substrate. Observations under natural and ultraviolet light indicated that penetration was extremely limited. In contrast, the oil penetrated the upper 2 to 4 cm of soil in the control plot. Thus, polyvinyl acetate and xanthan gum did provide protection against significant oil penetration compared with the control plot. The water spray system appeared to prevent penetration in those areas of the plot where the water flow was continuous, but areas left unprotected were affected in a manner similar to the control plot.

Xanthan gum was ranked as the best short-term surface treatment agent for Arabian crude oil because it worked slightly better than polyvinyl acetate when the oil was flushed from the substrate. Over the long term (a 3-day period), polyvinyl acetate proved the most effective because it persisted. The water spray system was ranked third because of the limited protection afforded.

The surface collecting agent was tested using Arabian crude oil only. The application method consisted of spraying approximately 1 liter of the agent into the water ahead of the approaching oil. In calm water, the agent kept the oil from advancing toward the marsh plot, contracting the slick seaward against the inner boom. Turbulence caused by waves broke up and dispersed the slick, and some of the slick washed shore. Once in droplet form, attempts to reunite the slick with more of the agent were unsuccessful. In addition, the oil droplets were difficult to recover with the type of polyethylene sorbents used.

#2 Fuel Oil—

The #2 fuel oil tests were conducted using four 1.2-by-3-meter marsh plots. Using the rotary pump, approximately 23 liters of polyvinyl acetate were sprayed on one plot and 57 liters of xanthan gum on another. The other two plots were a control and the water-spray section. In all, 190 liters of #2 fuel oil were used in this test, which meant that each marsh plot (and beach plot) was exposed to an average of approximately 24 liters of oil. Water was used to force the oil onto the salt marsh because of the relatively low tide. Consequently, as in the other tests, only the outer marsh fringes were exposed to the #2 fuel oil. Table 11 summarizes the results of this test.

In contrast to the #6 fuel oil and Arabian crude oil tests, polyvinyl acetate was found to be the most effective agent in protecting the salt marsh from #2 fuel oil contamination. Most of the oil was readily flushed from the substrate and vegetation immediately following contamination. Flushing the xanthan-gum-treated plot appeared to enhance oil penetration into the substrate by removing the protective layer of the agent. This was not the case with the polyvinyl-acetate-treated plot. Polyvinyl acetate appeared to provide an effective protective film. The control plot had extensive substrate penetration.

Both polyvinyl acetate and xanthan gum were effective in preventing accumulation of the oil on vegetation. After flushing, the shiny or oily appearance had been significantly reduced or had disappeared. The control plot, on the other hand, still appeared shiny even after flushing, indicating the persistent nature of the oil.

Flushing the polyvinyl-acetate- and xanthan-gum-treated plots with low-pressure water caused the polyvinyl-acetate film to be disrupted on the substrate and most of the xanthan gum to be flushed from both the substrate and vegetation. These observations are similar to those for the #6 fuel oil and Arabian crude oil tests. The natural deterioration of both of these agents was also the same as that observed in the other tests; the polyvinyl acetate was persistent, affording at least 50% protection over a 3-day period on both substrate and vegetation, while the xanthan gum had all but disappeared after one tidal cycle.

The water-spray system did show some promise in preventing oil substrate penetration in those areas where water flow was uniform. However, as before, the protection was not complete because of the inability to achieve a uniform flow on the irregular substrate. The water-spray system did appear to work better with the #2 fuel oil than with either the #6 fuel oil or the Arabian crude oil because of the lighter nature of the oil. Large waves did cause transport and deposition of some of the oil behind the spray, but this was observed in all oils tested. Little protection was provided to the vegetation except near the base of the plant.

The three marsh plots protected by surface treatment agents were not as contaminated as the control plot. The most effective agent over both the short and long term was polyvinyl acetate. By providing an effective barrier after drying, and consequently maintaining at least 50% of the film over a 3-day period, polyvinyl acetate shows promise as a surface treatment agent. Xanthan gum prevented significant oil penetration during the short term, but upon flushing and removal of the agent, oil that remained or was reintroduced in the next tidal cycle was able to penetrate the substrate. For this reason the water-spray system, which can be left in operation for long periods of time, was ranked above xanthan gum as a long-term agent for marsh protection from #2 fuel oil.

SUMMARY

Of all agents tested, polyvinyl acetate shows potential for providing the best overall protection from all oils tested. The #6 fuel oil and Arabian crude oil tests suggest that xanthan gum works best as a short-term agent and polyvinyl acetate best as a long-term agent. For #2 fuel oil spills, polyvinyl acetate appeared to be both the best short-term and the best long-term agent to use. Over the long term, the water-spray system appears more effective against #2 fuel oil than xanthan gum because of the recontamination problem encountered when xanthan gum is flushed.

Polyvinyl acetate was more persistent than xanthan gum on both the substrate and marsh vegetation. Xanthan gum had almost completely disappeared after flushing and one tidal cycle. Polyvinyl acetate was still at least 50% present on the substrate and 50% to 75% present on the vegetation 3 days after application. Because the water-spray system could be used continuously, it would have to be considered the most persistent of any agent tested. However, because of the irregular topography of the marsh, a uniform water film was not possible. This was especially true for the vegetation; it was very difficult to spray the entire plot so that all plants were covered. Therefore, the primary effectiveness of the water spray was on the substrate, and its best use was against #2 fuel oil.

The surface collecting agent was tested with Arabian crude oil only. Under nonturbulent conditions the surface collecting agent effectively prevented oil from coming ashore when it was applied just in front of the advancing slick and to the marsh. When wave-induced turbulence occurred the contained oil slick broke up into small spots and the collective effect could not be reestablished by reapplications of the collecting agent and the vegetation became contaminated. The oil-absorbing properties of the polyethylene sorbent were affected by the surface collecting agent and oil adherence to sorbent was impaired. However, the oil-contaminated vegetation was easily cleaned by low-pressure flushing and the surface collecting agent appeared to reduce oil adherence to marsh plants.

Protection Effectiveness

Four major criteria were applied in the evaluation of the relative effectiveness of polyvinyl acetate and xanthan gum:

- degree of substrate penetration by the oil
- ease of removal of the oil by flushing
- removal of agent by flushing
- natural degradation of the agent over time

The last three criteria were used in the evaluation of agent effectiveness on the marsh substrate and vegetation of *Spartina alterniflora*. Since no agents were applied to the control plot, only penetration and oil removability could be used as criteria.

The water-spray system and the surface collecting agent were evaluated according to criteria different from those for polyvinyl acetate and xanthan gum because of the nature of the application and the means of protection afforded. Each is designed to prevent oil from reaching the marsh grass. The criteria used to evaluate these agents was their effectiveness under nonturbulent and turbulent water conditions.

Modifications

Modifications will be necessary to make the water-spray system more effective in preventing marsh contamination. The spray should be more uniform in order to protect both the vegetation and the substrate from oil contamination. The system should be designed in such a way that the nozzles or water openings cannot be clogged by sediment picked up by the intake hoses. A solution to both problems may be provided by a water diverter placed over the open holes in a pipe. If such a system could be designed, water spray might prove to be an effective, efficient, and inexpensive means of protecting salt marshes. However, if a spill threatened a long expanse of shoreline, a spray system would require a rather elaborate distribution system. Deployment of such a system would be another problem.

For applications of polyvinyl acetate or xanthan gum on a larger scale, development of a higher-volume application system may be necessary. The experience gained using the rotary pump indicates that such a system could be designed.

A polyvinyl-acetate formulation that would decrease the drying time on wet marsh substrates and vegetation should be investigated. In the event of a spill, it may be necessary to have the agent sprayed on and dried in a short period of time. This would be particularly important under cloudy sky conditions. When the sky is overcast, the temperature cool, or a slight drizzle falling, drying time for the polyvinyl acetate is extended considerably. Polyvinyl acetate must cure and acquire a plastic consistency to provide marsh protection.

APPENDIX A

LITERATURE REVIEW

SURFACE TREATMENT AGENTS

A literature survey was conducted by Texas Research Institute, Inc. (TRI) to provide a basis for analyzing the results of previous tests of surface treatment agents and comparing their effectiveness. Sources of information included the final reports of four previous API-sponsored studies (by Exxon, Shell, and Tracor), other reports, technical product bulletins, and personal communications with suppliers and other informed individuals. It was frequently impossible to objectively compare the agents and methods used in the previous work because of different testing techniques. Therefore, where possible, estimates and judgments made by TRI on the previous work were substituted for hard data so that relatively complete data on each agent could be presented and compared.

The nine surface treatment agents reviewed are listed below. (In the initial phase of this study 10 surface treatment agents were suggested for the literature review. The tenth agent, polyvinyl acetate with a degradation accelerator, was to have been developed through an expanded scope of the program. This was not undertaken.)

* polyvinyl acetate (Borden Polyco 694)

* xanthan gum (Biopolymer 9700)

* citrus pectin

* _Micrococcus_ _cerificans_

* sodium silicate (waterglass)

* borate-silicate mixture

* surface collecting agent

* dispersing agents

* water

All of the surface treatment agents were compared (using data compiled from the literature review) for mechanism of action and effectiveness on the substrates on which they were tested and for limitations on use imposed by climatic factors and environmental impacts. A summary of the results of the literature survey is given in the following paragraphs and shown in Table A-1.

Polyvinyl Acetate

Polyvinyl acetate is available in a 55% aqueous suspension that can be sprayed without dilution from a spraying system. For an effective solid film, the coating must dry to allow the film to cure. This means that ultimate solidification will not occur in wet weather. The cured film is highly effective in preventing oil staining or penetration; it is quite stable and lasted for several days under the wave action of the test conditions. When sprayed, the material gives a milky-white color to the test beach. Upon drying, the film is clear and firm; rocks and wood appear varnished. However, the film will turn white if it becomes wet.

Xanthan Gum

Polysaccharide/xanthan gum is a high-molecular-weight biopolymer produced by fermentation by the microorganism *Xanthomonas campestris*. It is available commercially in dry form or in a concentrated solution. In tests it was sprayed on as a 0.5% aqueous solution and allowed to dry. Xanthan gum forms a "soft" film because it is swollen with water. Such a hydrophilic film is not attractive to oil staining and penetration. However, because of the hydrophilic nature of the film, it is easily washed away. Exxon reported that most of the film was washed off by wave action within an hour. It was tested on river rocks and marsh grass and was judged to be effective in protecting them against oil contamination.

Citrus Pectin

Polysaccharide/citrus pectin is a complex carbohydrate with limited water solubility but with water-attracting groups. The mechanism of action of citrus pectin is similar to that of the xanthan gum. A 1% solution was sprayed on river rocks and marsh grass in the lab tests. The advantages and disadvantages of citrus pectin as well as the test results are essentially the same as those for xanthan gum.

Borate-Silicate Mixture and Sodium Silicate

Borate-silicate mixtures and sodium silicate were investigated separately by Shell Development Company. Both were found to be effective in protecting rocky beaches. Shell did not recommend borates because of reports of its toxicity to aquatic flora. In Shell's tests with sodium silicate and sodium borate, 1%-3% solutions of each were sprayed on scale beaches. The agent dried to form an inorganic film. The film was not attractive to oil but was readily wet by water and was effective in protecting rocks, but not sand. To be effective, the film must have time to dry; this limits its application. However, when silicates and borates are sprayed on sand wet with ocean water, they form a soft gelatinous film that may be effective in protecting sandy beaches. This approach was not fully investigated. The silicates form highly

TABLE A-1. SUMMARY OF RESULTS OF LITERATURE REVIEW OF SURFACE AGENTS

Agent Type	Mechanism	Form/Application	Possible Limitations	Summary of Previous Investigations		
				Sand	Rocks	Marsh Grass
Polyvinyl acetate	Solid film	Synthetic polymer/conc. (55%) aqueous suspensions; sprayed on, high-pressure, airless sprayer; available dry	Removal, color, rainy/freezing weather, must have 1 hr to dry before it is effective	Effective	Effective	Not tested
Surface collecting agent	Has greater spreading force than oil; liquid monomolecular layer	Long-chain alcohols in organic solvent (water insoluble)	Short duration, loss of effectiveness, might need continuous supervision	Effective in lab and beach tests	Effective in lab and beach tests (less effective on dry rocks)	Not tested
Dispersing agent	Adjusts interfacial surface tension; develops micelles of oil in water	Nonionic detergent/aqueous solution (6%)	Must be applied directly to oil, large volume required	Not tested	Not tested	Not tested
Xanthan gum	Soft polar film	Sprayed on, dilute (0.5%) aqueous solution; available as dry powder or concentrated solution	Short duration, 1 hr drying time necessary	Not tested	Effective on dry rocks	Possibly effective
Citrus pectin	Soft polar film	Sprayed on, dilute (1%) aqueous solution; available as dry powder	Short duration, 1 hr drying time necessary	Not tested	Effective on dry rocks but less effective than xanthan gum	Possibly effective
Borate-silicate mixture	Solid film (if cured)	Inorganic coating, dilute (1-3%) aqueous solution; sprayed on	Toxicity?, pH, drying time necessary	Not effective	Effective	Not tested
Sodium silicate	Solid barrier (if cured)	Inorganic coating, dilute (1%) aqueous solution; sprayed on	Toxicity?, pH, drying time necessary	Not effective	Effective	Not tested
Micrococcus cerificans	Unknown	Freeze-dried, (3%) aqueous suspension; sprayed on, garden sprayer	Not commercially available, large preparation effort, half life, drying time necessary	Not tested	Effective on dry rocks, less effective than polysaccharides	Not tested
Water film	Liquid film	Sprinkler system	Continual application required (countercurrent), equipment costs	Not tested	Not tested	Not tested

alkaline solutions, which may be an environmental problem.

Micrococcus Cerificans

The soil bacterium *Micrococcus cerificans* was cultered by Exxon researchers and tested in three forms - live, freeze-dried, and spray-dried. Only the spray-dried form could be seriously considered because the other two pose storage problems. The spray-dried material was applied to rocks as a 3% aqueous solution and was moderately effective in protecting against oil contamination. Its mechanism for protection was not explained. The material was not effective in cleaning rocks previously contaminated with heavy oils. *Micrococcus cerificans* is not available in commercial quantities. This, along with its lack of effectiveness, essentially eliminated it from further consideration as a surface treatment agent.

Surface Collecting Agent

A surface collecting agent is highly effective in limiting the spreading of oil over water by forming a monomolecular layer on the water surface. The chemical is sprayed directly onto the beach or into the water between the oil and the beach. It may be applied in wet weather, but it solidifies at 2.2°C, which places a low-temperature limit on its use. It is effective in protecting sand and wet beaches, but less effective in protecting dry rocks and wood. It also appears effective in cleaning previously contaminated beaches. Its protection is of short duration, and it must be applied after each high tide.

Dispersing Agent

A nonionic dispersing agent uses the agitation of the surf to mix the dispersant with oil and water and its use is rarely limited by weather conditions. The mechanism of action depends on the dispersant interacting with oil to form dispersed oil micelles. It was reported that this dispersant is thought to be effective because it disperses the oil and carries it back out to sea in the undertow before it can adhere to the beach. It is possible that almost continual application will be required.

Flowing Film of Water

All of the API reports on chemical-agent shoreline treatment methods mentioned that oil does not stain wet beaches or rocks. Indeed, most contamination of beaches occurs when oil is stranded by receding tides and left on the upper intertidal zone. This would suggest the use of an oleophobic mechanism of shoreline protection - wetting all surfaces to form an oil-repelling liquid film. A sprinkler system could be used to keep a continual countercurrent of water wetting a shoreline and washing oil back into the surf. Although this method has not been evaluated specifically as a surface treatment agent, a flowing film of water shows some promise for protection of shorelines from oil contamination.

INFLUENCE OF CLIMATIC CONDITIONS

Table A-2 details the influence of climatic conditions on each of the surface treatment agents. Judgments by TRI were based largely on the previous laboratory experiments and logical extrapolations from these experiments. For instance, rain is obviously detrimental to materials that must dry to form a film or that are quite soluble and easily washed away. Low temperatures (freezing) prevent the spraying of aqueous solutions and the curing of the film-forming agents. Likewise, low temperatures prevent the use of the organic-solvent-based surface collector because it solidifies below 2.2°F. Thus, none of the surface treatment agents considered here is readily adaptable to cold climates.

Tidal and wave action is especially detrimental to the collecting agents and to the more soluble agents, such as the polysaccharides, but aids dispersing action. Hence with some agents treatment will be needed at least after each tidal cycle.

High winds are a problem for all agents because they interfere with spray application.

ENVIRONMENTAL IMPACT OF AGENTS

Table A-3 presents the probable environmental impact of each of the surface treatment agents. The "Appearance" column refers to the visual effect and feel of the agent on the shoreline, i. e. , whether it modifies the appearance and texture of the shorelline enough to be aesthetically unacceptable. Toxicity data were taken from published reports and technical information and include references both to organisms on the shoreline and to people who apply the agent. An additional factor in toxicity is the secondary effect of the agent. For example, if the coating is impermeable to air and water and if the agent is not toxic, subsurface species can exist. The surface collector tested is listed as low in toxicity because only small quantities are allowed by regulation to be used; the concentrated solution requires care and protective clothing for the application process. The toxicity of borates and silicates is somewhat questionable; however, it is doubtful that their toxicity is high enough to be of concern once the film has cured.

Estimates of the duration of the agents on the shoreline after the need for shoreline protection is over are based largely on laboratory experiments done in the previous studies. Thus it is impossible to accurately predict the duration on a natural shoreline subjected to sun, wind, rain, surf, tides, and other factors. The solid film-forming agents might last for several days or even weeks. The soft film-forming agents and surfactants would probably be washed away by surf action within hours.

APPLICATION TECHNIQUES

In the previous studies, agents were either sprayed or poured on the test substrates. All the agents except polyvinyl acetate could be applied with a portable garden-type sprayer. Due to an undesirable foaming that occurred

TABLE A-2. INFLUENCE OF CLIMATIC CONDITIONS ON SURFACE TREATMENT AGENTS

Agent	Sun	Wind	Rain	Temperature	Tidal Action	Wave Action
Polyvinyl acetate	Aids in drying film; may aid in degrading film	Adversely affects spraying; generates detrimental surf action; aids drying	Prevents drying of film; may wash away spray	High temperature aids film drying; low temperature may prevent spraying and/or drying	May erode film	Degrades film
Surface collecting agent	No effect	Adversely affects spraying; generates detrimental surf action	Works best on wet sand and surfaces	Solidifies below 2.2°C	Must renew treatment between tides	Detrimental effect
Dispersing agents	Unknown	Adversely affects spraying; generates beneficial surf action	Probably helps dispersing action	Unknown	No effect	Aids dispersion action
Xanthan gum	Aids drying	Adversely affects spraying; generates detrimental surf action; aids drying	Prevents drying; washes off agent	High temperature aids drying; low temperature may prevent spraying and/or drying	Film quite soluble, must be renewed between tides	Dissolves film
Citrus pectin	Aids drying	Adversely affects spraying; generates detrimental surf action; aids drying	Prevents drying; washes off agent	High temperature aids drying; low temperature may prevent spraying and/or drying	Film quite soluble, must be renewed between tides	Dissolves film
Borate-silicate mixture	Aids drying	Adversely affects spraying; generates detrimental surf action; aids drying	Prevents drying; washes off agent	High temperature aids drying; low temperature may prevent spraying and/or drying	Little effect	Little effect
Sodium silicate	Aids drying	Adversely affects spraying; generates detrimental surf action; aids drying	Prevents drying; washes off agent	High temperature aids drying; low temperature may prevent spraying and/or drying	Little effect	Little effect
Micrococcus cerificans	Aids drying	Adversely affects spraying; generates detrimental surf action; aids drying	Prevents drying, washes off agent (very soluble)	High temperature aids drying	Must renew treatment between tides; very soluble	Dissolves agent
Water	No effect	Has drying effect	May help	Low temperature may prevent use	No effect	No effect

TABLE A-3. PROBABLE ENVIRONMENTAL IMPACT

Agent	Appearance	Toxicity*	Duration
Polyvinyl acetate	Hard-coated white surface when wet	Nontoxic, air and water permeability unknown	Estimated long duration
Surface collecting agent	None	Very low toxicity, care required in application	One tide cycle or less
Dispersing agents	None	Depends on dispersant used	One tide cycle or less
Xanthan gum	Clear, gels with water	Nontoxic	Approximately one tide cycle
Citrus pectin	Clear, gels with water	Nontoxic	Short duration, less than 1-2 hours in contact with water
Borate-silicate mixture	Glassy coating on rocks (probably gels with sea water	Questionable; borates may be poisonous to aquatic flora and are on list of hazardous substances, Federal Register, V.39, August 1974	Short duration, less than 1 hour in contact with water
Sodium silicate	Glassy coating on rocks, gelatinous coating on sand when sea water added	Silicates on list of hazardous substances, Federal Register, V.39, August 1974	Short duration, less than 1 hour in contact with water
Micrococcus cerificans	None	Probably nontoxic	Short duration, possibly 1-2 hours
Water	None	None	--

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* Toxicity data were taken from published reports and technical information and refer both to organisms on the shoreline and to people who apply the agent.

when spraying polyvinyl acetate with air-pressure spray equipment, a commercial high-pressure airless spray unit was used.

In some of the mock-shoreline experiments, the test oil was applied directly to dry substrates by brushing or spraying. Because oil is transported to the shoreline on the surface of water, this practice will not be continnued in future testing.

EVALUATION METHODS

Methods used to evaluate the effectiveness of the surface treatment agents tested include the following:

- * visual-subjective judgment (all studies)
- * photographic record (all studies)
- * analysis of residual oil by measuring oil removed from test bed (Shell studies)
- * analysis of penetration of oil through the agent into porous substrates (Shell and Tracor)
- * measurement of wetting and spreading of oil on treated and untreated substrates (Tracor)

In addition, some simple laboratory tests were employed by Tracor to evaluate other parameters, such as film-forming ability and solubility in oil and water, affecting the suitability of film-forming agents. Most of the evaluation methods used in the previous studies can be adapted for future work. Unfortunately, none of the previous studies found suitable methods for directly determining how much agent remained on a test substrate after exposure to wave action or how much oil remained on the substrate after cleanup.

COST CONSIDERATIONS

Table A-4 presents a breakdown of costs associated with the use of each agent. The costs are estimated for both a 2889-square-meter area and a 50,000-square-foot area of treated beach. These areas are equivalent to about 1 km and 1 mile, respectively, of shoreline that is treated over a 3.1-meter-wide tidal zone.

The costs of agents vary from 13 cents per kg (6 cents per pound) to over $220 per kg ($100 per pound), depending in part on commercial availability. However, because the quantity needed must also be considered, a more realistic evaluation of agent cost can be found in the fourth column, which lists the cost of agents needed for either 1 km or 1 mile of shoreline treated. The effort required to prepare the agent for application is included in the table, although this is not a factor for most agents since they are produced and can be stored in a usable form. Column 7, Application Cost, includes labor and

TABLE A-4. ESTIMATED COST

Agent	Material Cost	Quantity Needed*	Material Cost	Stability	Preparation Effort	Application Cost**	Agent Cleanup Cost
Polyvinyl acetate	60¢/kg (27¢/lb) in solution	1268.3 kg/km (4500 lb/mi) as 55% suspension; 1317.2 liters/km (560 gal/mi)	$754.97/km ($1,215/mi)	Stable (test for 2-yr storage)	Nil	Single application $310-$621	Unknown
Surface collecting agent	$2.44/liter; ($9.25/gal); 208.2-liter (55-gal) drums	235.2 liters/km (100 gal/mi) for real-world test; 32.9 liters/km (14 gal/mi) for lab test	$574.77/km ($925/mi)	Stores indefinitely	Nil	Multiple applications anticipated, $621-$932	Nil
Dispersing agents	$1.40/liter ($5.30/gal); 208.2-liter (55-gal) drums	2 to 10 parts per 100 parts of oil; assume 1176.0 liters of oil/km (500 gal/mi)	$77.67/km ($125/mi)	Stores indefinitely	Nil	Continuous applications anticipated (small craft necessary), $932-$1553	Nil
Xanthan gum	$4.50/kg ($2.50/lb)	6.5 kg/km (23 lb/mi) - dry weight 1282.4 kg/km (4550 lb/mi) - 0.5% solution	$37.28/km ($60/mi)	Stores dry - stable if dry	Dissolves slowly, high-shear mixing required	Multiple applications anticipated, $621-$932	Unknown
Citrus pectin	$7.72/kg ($3.50/lb)	13.8 kg/km (49 lb/mi) - dry weight; 1381.1 kg/km (4900 lb/mi) - 1% solution	$105.63/km ($170/mi)	Stores dry - stable if dry	Dissolves slowly, high-shear mixing required	Multiple applications anticipated, $621-$932	Unknown
Borate-silicate mixture	13¢/kg (6¢/lb); dry powder	62.0 kg/km (220 lb/mi) - dry weight; 6468.3 liters/km (2750 gal/mi) in solution	$12.43/km ($20/mi)	Stores dry	Difficult to put into solution	Single application $310-$621	Unknown
Sodium silicate	15¢-26¢/kg (7¢-12¢/lb)	62.0 kg/km (220 lb/mi) - dry weight; 6468.3 liters/km (2750 gal/mi) in solution	$15.53/km ($25/mi)	Stores dry - hygroscopic	Difficult to put into solution	Multiple applications anticipated, $310-$621	Unknown
Micrococcus cerificans	Not commercially available; $220 to $2200/kg ($100-$1000/lb)	42.3 kg/km (150 lb/mi) - dry weight	$8,077.83-$9,320.67/km ($13,000-$15,000/mi)	Washes off easily, limited storage except for spray-dried form	Must be mixed with water	Multiple applications anticipated	None
Water	None	Unknown	None	Infinite	Spray system requires installation	Spray system must be maintained, $1500 install., $500 maintenance	Removal of spray system $1500

* Approximately 2889 square meters to be treated per km (50,000 square feet per mile).

** Labor and equipment for first km (excluding standby).

equipment for the first km of application. Subsequent shoreline coverage would be considerably less expensive. Excluded from application costs are standby costs, observation personnel above first-level supervision, communication systems, elaborate equipment, etc. The cleanup costs are unknown for most agents because their lifetimes are also unknown. It is hoped, however, that these costs can be minimized.

Table A-4 shows that agent and application costs are most significant. The polyvinyl acetate has a moderate to high initial cost, but only one application is required. The disadvantage of surfactants is that multiple or possibly continuous applications are required, but film removal is unnecessary. Xanthan gum and citrus pectin will be somewhat costly to prepare because it is difficult to form viscous solutions in water and because mixing equipment is needed. Micrococcus cerificans has a prohibitive purchase cost because it is not commonly available, and it requires special laboratory preparation. Water itself has no cost because it will be drawn from the sea, but equipment is necessary to provide a continually flowing film. Pipes and pumps to cover 1.6 km are estimated at $10,000; these are, of course, reusable.

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APPENDIX B

PRELIMINARY AGENT EVALUATION TESTS

LABORATORY EVALUATION

Three types of laboratory tests on surface treatment agents were undertaken: (1) screening tests on the basis of solution and film properties (solubility, film formation, etc.); (2) small-scale tests of beach protection on mock beaches; and (3) percolation tests (on three of the agents) for effectiveness in preventing oil seepage. The tests are described in this appendix, and the results for each agent are given after the descriptions of each test. The agents tested are listed below:

* polyvinyl acetate - synthetic film-forming agent (Borden Polyco 694 and 2113 and Union Oil Amsco 3006 and 3011 were tested)
* sodium silicate - inorganic film-forming agent
* borate-silicate mixture - inorganic film-forming agent
* xanthan gum - natural polymeric film-forming agent
* citrus pectin - natural polymeric film-forming agent
* dispersing agent - chemical that interacts with oil to form dispersed oil micelles (Dispersant A was tested)
* surface collecting agent - chemical that reduces oil spreading
* water - continuous film of flowing water

Synergistic effects with the surface collector and two of the film-forming agents, xanthan gum and polyvinyl acetate, were also investigated.

Laboratory Tests

The film-forming surface treatment agents were subjected to screening tests to determine their solution characteristics, film-forming ability, film solubility, etc., before their effectiveness on mock beaches was tested. The test methods are described below, along with the results for each agent. Not all agents are listed for each test because not all tests apply to each agent. For instance, Polyco 694 was purchased in a 55% water solution. Hence there is no need to test it for solubility problems. Results will be listed for all agents for which the test is applicable and are shown in Table B-1. Further testing of the borate-silicate mixture was not attempted because of its solution instability and failure to produce a detectable film.

Solution Process--

Solutions of desired concentrations were prepared with tap water. The amount of heating, agitation, and time required to effect solution were noted as well as special techniques required and the stability of the solution once formed.

1. Citrus pectin was difficult to dissolve. In order to make a 0.5% solution (by weight), the solution had to be heated to 50° C. Heating to near boiling (along with vigorous stirring) was necessary to effect a 1.0% solution. The solutions are viscous; the 1% solution has an almost jellylike consistency at room temperature.

2. Xanthan gum was easy to put into solution in both 0.5% and 1% concentratins if cold water was stirred and the powdered gum added to the vortex. The solutions became viscous as the powder became hydrated. Viscosities were approximately the same as with the citrus pectin.

3. Sodium silicate was impossible to dissolve directly to form 1%-3% solutions. According to literature on the material, sodium silicate is more soluble in concentrated solution than in diluted solution. Thus a 50% commercial sodium-silicate solution was used as a source of dissolved silicates, and dilutions were made to form 1%, 2%, and 3% solutions. These solutions showed some cloudiness after standing for several days.

4. Borate-silicate mixture (sodium silicate/sodium borate) solutions were initially made by adding the required weight of borate to the sodium-silicate solution. However, this is not a simple process. Addition of dry sodium borate to the concentrated sodium silicate resulted in the formation of a glassy precipitate on the surface of the silicate which would not dissolve even when heated. (Heating caused flocculation of undissolved borate but did not affect the glassy surface.) Solution was effected by first dissolving the borate in water and then adding this solution to a diluted silicate solution. Using this technique, solutions containing equal portions of silicate and borate salts in the total amounts of 1.0%, 2.0%, and 3.0% were prepared. After one day some cloudiness and precipitation were noted in all silicate solutions. The 3.0% solution turned completely into a white gelatinous suspension after one day.

Film Formation--

Microscope slides were dipped two-thirds of their length into a solution of the agent and allowed to dry. The appearance of the film (if any) was noted and its thickness measured with a micrometer.

TABLE B-1. SOLUTION AND FILM PROPERTIES OF SELECTED FILM-FORMING AGENTS

Agent	Citrus Pectin	Xanthan Gum	Sodium Silicate	Borate-Silicate Mixture
Concentration range	0.5%-1.0%	0.5%-1.0%	Undetectable	1%-3%*
Preparation of solution	Heating required	Dissolves readily	Difficult (see text)	Difficult (see text)
Characteristics of solution	Viscous to jellylike	Viscous to jellylike	Becomes cloudy after a few days, pH: 9-11	3% solution gels overnight
Film formation on glass slides	Dipped - very thin but detectable; sprayed - fair-good	Dipped - same as pectin; sprayed - better than pectin	Dipped - undetectable; sprayed - not tested	Dipped - undetectable; sprayed - blotchy, isolated crystal formation
Film formation on screens (dipped)	Good	Good	No film formed	No film formed
Properties of films	Poor-fair	Good	None formed	None formed
Sprayability with conventional paint sprayer	OK	OK	OK	OK

* 50:50 ratio of sodium silicate to sodium borate, with total concentration in the range of 1% to 3%.

1. Citrus pectin at a 0.5% solution formed a very thin film. Slide appeared slightly dirty.

2. Xanthan gum at a 0.5% solution did not form a complete film on slide but seemed to be thicker than the 0.5% solution of citrus pectin. The 1.0% solution formed a cloudy, thin film (25 microns).

3. Sodium silicate and borate silicate - no detectable or observable film on the microscope slides.

Film Solubility—
The slides from the film-formation test were placed in beakers of salt water and agitated gently. The appearance of the film was noted as well as its durability.

Dip-formed films of citrus pectin on glass slides could be readily removed in 30 minutes by immersion in salt water, especially with slight agitation. Those films made from xanthan gum yielded films that remained after overnight immersion.

Since dip-formed films of sodium-silicate and silicate-borate solutions could not be detected, the immersion tests on them gave no data.

Screen Film Formation and Penetration—
Small squares of fine-mesh copper screen were dipped into each test solution and allowed to dry. The film that formed (if any) was evaluated as to appearance and continuity. Continuous films were tested for water and oil penetration by simply placing a few drops of water (or oil) on the surface and checking for its penetration to the other side.

1. Citrus pectin at a 0.5% solution formed an incomplete film but covered over 70% of screen. 1.0% - complete film.

2. Xanthan gum - same as citrus pectin; 1.0% solution was particularly good.

3. Sodium silicate and borate silicate - no films were formed; agents crystallized on screen.

Sprayability and Sprayed Film Formation—
The test solutions were sprayed onto 10x10-cm glass plates to test for spray characteristics. Pressure necessary for spraying, the type of spray pattern, size of droplets, coverage, etc., were noted.

Citrus pectin, xanthan gum, and borate-silicate films were prepared by spraying the solutions using a conventional compressed-air-operated (4.2 kg per sq cm, 60 psi) paint spray gun. All solutions could be sprayed effectively. Observations of the films were as follows:

1. The 3.0% borate-silicate solution did not form a complete film. There were isolated areas of crystals.

2. The 1.0% solution of xanthan gum gave a more complete film than that of the borate-silicate solution. Film was complete in the center of the glass plate. The coating density decreased as the radial distance from the center increased.

3. The film of 0.5% solution of xanthan gum was barely observable. It had the same density vs. radius relation as in the solution.

4. The film of 0.5% solution of citrus pectin was complete but not very dense. Blotches formed near the perimeter of the plate.

5. The film of 1% solution of citrus pectin was complete. It formed concentric areas of low-density coverage that were separated by ridges or barriers of slightly higher density. Blotches formed at plate edges.

Film Solubility-Durability—
Dry films on the glass plates from the sprayability tests were used. The slides were propped at a 45-degree angle below a buret filled with salt water. Water was dropped from a height of approximately 20 cm onto the film, and its effect was noted both at the point of impact and on the runoff area.

1. Borate-silicate 3.0% solution - Water droplets appeared to wash away any film that may have been present.

2. Citrus-pectin 1.0% solution - The citrus pectin film migrated to the lowest edge of the glass plate with the addition of water droplets, but accumulation at the edge was not as great as with the accumulation from the 1.0% citrus- pectin solution.

3. Xanthan-gum 0.5% solution - The xanthan gum film became swollen with the addition of water but it did not migrate. After drying, the film was intact.

4. Xanthan-gum 1.0% solution - Parts of the film from the 1.0% xanthan-gum solution migrated slightly toward the edge of the plate, but most of it remained intact.

Mock-Beach Tests

Mock beaches were constructed in approximately 75-cm-square plastic pools that were mounted in a rocking mechanism. The beach was constructed of sand and gravel, with some larger rocks and pieces of wood added to the surface. The total surface area was 0.427 sq meters. Water was added to the pool, and the rocking mechanism simulated wave action. The durability of film-forming agents was evaluated before any oil was added to the pool. As a result, several agents were not considered for further testing because they failed the durability test. Surfactants were also tested in the mock-beach tests. There was a control mock beach for each of the mock-beach tests. Detailed results of the mock-beach tests are given in Table B-2.

TABLE B-2. RESULTS OF MOCK BEACH TESTS

Agent Tested	Application Method	Film Durability	Film Resistance to Oil
Citrus pectin, 1% solution in water	600 ml at 2.8 kg/sq cm (40 psi). Beach dried 24 hours with IR heat lamp. Little or no film was evident.	No film characteristics apparent; agent-protected sand was indistinguishable from that in the control; testing was discontinued.	Not tested.
Citrus pectin, 2% solution in water	600 ml at 4.2 kg/sq cm (60 psi). Drying with IR heat lamp for 7 hours resulted in a hard crust.	Rapid loss of film integrity, considerable erosion, development of holes, etc. Film not apparent within 5-minute test duration. Testing was discontinued.	Not tested.
Xanthan gum, 1% solution in water	600 ml at 4.2 kg/sq cm (60 psi). Beach dried 24 hours with IR heat lamp. A "crusty" film formed.	Became hydrated, showing wrinkles and bubble formation almost immediately after addition of synthetic sea water; film remained intact for the duration of the test.	500 ml of Kuwait crude applied. After 2 hours of the test the xanthan-gum-protected beach was compared to a control beach. The xanthan-gum film had dissolved from the wash line and below. No appreciable difference in cleanability between the xanthan-gum beach and the control beach, although the agent-protected beach did not erode from the wash-bottle spray as much as the control beach did.
Xanthan gum, dry powder	154 g of xanthan-gum powder sprinkled over a wet beach and, after 30 minutes, sprayed with a water mist. Dried 6.5 hours with IR heat lamps to a crust that shrunk and started to roll up due to an adhesive failure with the beach itself.	Almost immediate hydration and color change of the film. Bubbles and wrinkles soon formed, but film remained intact for the duration of the test.	500 ml of #2 fuel oil added. Film degraded severely within 2 hours. Cleanability was similar to that of control beach. Oil penetration detected at all levels.
Xanthan gum, dry powder	96 g of xanthan-gum powder was sprinkled over a wet beach. In this test, the slightly hydrated powder was not dried, and the film durability test was immediately started.	The synthetic sea water hydrated the xanthan gum to such an extent that patches of the very gelatinous material separated from the beach surface and started floating in the water. Testing was discontinued.	Not tested.
Xanthan gum, 1% solution in water	600 ml sprayed at 4.2 kg/sq cm (60 psi); beach not dried after application.	Coating remained thick (approximately 5 mm) in most areas, but washed off in spots after 1 hour.	500 ml of #2 fuel oil added. Film degraded at the water line after 2 hours. Oil penetration was noted at all levels.

(continued)

TABLE B-2 (Continued)

Agent Tested	Application Method	Film Durability	Film Resistance to Oil
Borden Polyco 694	950 ml of 694 was sprayed on the beach. This is a heavy coat. The beach was dried with the aid of IR heat lamps for approximately 20 hours. The film was still not dry all the way through, as was noted from the characteristic milky color of undried 694.	Film was slightly hydrated and water became slightly milky, bu' the film remained intact for the duration of the test.	500 ml of #2 fuel oil added. Oscillations continued for 2 hours. There was good cleanability of surface oil; UV light indicated oil permeation at all depths. Oil probably penetrated because so much was applied that it was difficult to get the film totally dry.
Borden Polyco 694	400 ml of 694 sprayed on the beach. This is a light coat. The film dried to a clear film after 20 hours under IR heat lamps.	Film remained intact for the duration of the test.	500 ml of #2 fuel oil added. Oscillations continued for 2 hours. The film exhibited good cleanability characteristics. UV light indicated only slight traces of oil increasing with the depth. This would indicate seepage around the sides of the film, i.e., at the interface between the film and the wall of the pool, rather than penetration through the main body of the film itself.
Borden Polyco 694	600 ml of 694 sprayed on the beach. This is a medium (standard) coat. Film dried to a clear film in 3.5 hours with aid of IR heat lamps.	Film turned from clear to slightly milky, but remained intact for the duration of the test.	500 ml of #2 fuel oil added. Oscillations continued for 4 hours. Film exhibited good cleanability characteristics. Traces of oil were found just under the film layer at the sand surface and at a 2.5-cm depth. Surface traces could have been due to pinholes in the film itself.
Borden Polyco 2113	500 ml sprayed on beach and allowed to dry.	After 30 minutes the film began to dissolve. Further tests discontinued.	Not tested.
Union Oil Amsco 3006	500 ml sprayed on beach and allowed to dry with aid of IR heat lamps.	Film dissolved within 30 minutes. Further tests discontinued.	Not tested.
Union Oil Amsco 3011	600 ml sprayed on beach. Dried to a clear film in 1.5 hours under IR heat lamps.	Film remained intact. Film did not get the milky hue that 694 gets when in contact with water.	500 ml of #2 fuel oil added and oscillations continued for 2 hours. Film exhibited good cleanability. Oil traces were detected at the sand surface under the film layer. Penetration into the beach was not detected.

(continued)

TABLE B-2 (Continued)

Agent Tested	Application Method	Film Durability	Film Resistance to Oil
Sodium-silicate solution, 50% in water	300 ml sprayed on beach. Dried with IR heat lamps to a crusty film.	Film dissolved immediately upon water contact. Further tests discontinued.	Not tested.
Sodium-silicate solution, 6% in water	400 ml sprayed on beach. Dried with IR heat lamps to a crusty film.	Film dissolved immediately upon contact with water. Further tests discontinued.	Not tested.
Sodium-silicate solution, 1.5% in water	600 ml sprayed on beach. Dried 1.5 hours with IR heat lamps.	Severe erosion within 10 minutes. Further tests discontinued.	Not tested.
Union Oil Amsco 3011 with surface collector as synergist	600 ml of 3011 sprayed on a mock beach. Dried under IR heat lamps for 1 hour. After the oil was added, 20 drops surfactant/collector applied at the wash line to see if there were any synergistic effects from combination of these agents.	Film remained intact.	500 ml of #2 fuel oil applied to synthetic sea water. Oscillations continued for 2 hours. After application of surfactant/collector a slight "herding" action took place. The confining effect of the herder dissipated with time due to the constant churning action of the waves. Oil penetration tests showed no change in protective ability of the film.
Xanthan gum with surface collector as synergist	150 g of xanthan-gum powder applied on wet beach. 40 drops surfactant/collector added at the wash line when the oil was added.	Xanthan gum dissolved almost immediately.	500 ml of #2 fuel oil added. There was a slight collecting action upon application of the surfactant/collector. The confinement of the oil decreased as the oscillation time increased; soon no herding effect was evident. UV exposures showed little or no surface oil residues, but significant residues at depths of 2.5 and 7.6 cm.
Dispersant A 2% solution in water	100 ml sprayed over the surface of the mock beach.	Not applicable.	500 ml of #2 fuel oil added and oscillations continued for 2 hours. UV analysis indicated oil penetration at all levels.
Dispersant A 10% solution in water	100 ml of this solution was sprayed over the surface of the sand.	Not applicable.	500 ml of #2 fuel oil added. This oil was emulsified within 5 minutes. UV exposures indicated oil penetration at all levels.

(continued)

TABLE B-2 (Continued)

Agent Tested	Application Method	Film Durability	Film Resistance to Oil
Surface collector	20 drops of surface collector were applied to the oscillating beach at the wash line	Not applicable.	500 ml of #2 fuel oil added to the sea water, oscillations continued for 2 hours. UV analysis indicated oil penetration at all levels.
Water (flowing over the beach in a continuous sheet)	Water continuously flowed from a spray head while excess was simultaneously removed.	Not applicable, although there was a considerable amount of beach erosion due to channels formed by flowing water.	Oil was detected at all levels. Test method probably does not simulate actual conditions.

Construction of Mock Beaches--

The same general construction procedures were used in building all of the mock beaches. Twenty liters of sand and gravel were added to each 75-cm-square plastic wading pool. The beach material was about 15.2 cm deep above the wash line and sloped gradually downward toward the other end of the pool (Figure B-1). The mock beaches were then settled with approximately 7.5 liters of salt solution (3.5% NaCl), which oscillated on the beach for 30 minutes. The excess sea water was then pumped out and, except when a dry application of xanthan gum was to be tested, some drying of the beaches was allowed to occur.

Depending on their physical nature, surface treatment agents were applied in one of two ways:

- If the agent to be applied was a dry powder, it was sprinkled on the beach surface through a 200-mesh U. S. standard sieve.
- If the agent was a liquid, it was applied to the beaches as a fine spray with a Sears Craftsman paint sprayer (700-ml capacity). The pressure (2.8 to 4.2 kg/sq cm, 40 to 60 psi) depended on the viscosity of the liquid being sprayed. The agents were then dried. The drying time was frequently accelerated with the aid of infrared heat lamps.

Test Procedures for Film-Forming Agents--

Tests of film durability and resistance to oil were used to evaluate the effectiveness of each surface treatment agent. The film-durability test determined the ability of the agent to withstand the effects of constant simulated wave action and sea water. If an agent did not function effectively in this test, no further testing of that agent was undertaken.

In the film-durability test, 5.6 liters of synthetic sea water (3.5% NaCl) was added to a mock beach on which an agent had been applied. Simulated wave action was initiated at a constant rate of 10 oscillations per minute for all tests and was continued for 30 minutes. Evaluation of each agent was based on the loss of film integrity (development of holes, tears, film dissolving) and on adhesive failure of the film on the beach (formation of bubbles or wrinkles between sand and film).

The oil-resistance test determined the degree of oil penetration on a mock beach and the ease with which any surface oil was removed. Only agents passing the film durability test were tested for resistance to oil. In the oil-resistance test, 500 ml of oil was added to the water of each beach, and wave action was continued at 10 oscillatins per minute for up to 2 hours. During this time the effects of the oil on the agent were observed. After wave action stopped, the oil/water mixture was drained. The ease with which the surface oil could be removed from the beach was then determined by washing the surface with a light stream of water from a wash bottle. The penetration of oil into the mock beach was determined by taking "blots" of the beach at the surface and at various depths within the beach column. These blots were taken with Whatman #1 filter paper, which when pressed to the beach column absorbs a representative sampling of any liquid within the beach column at

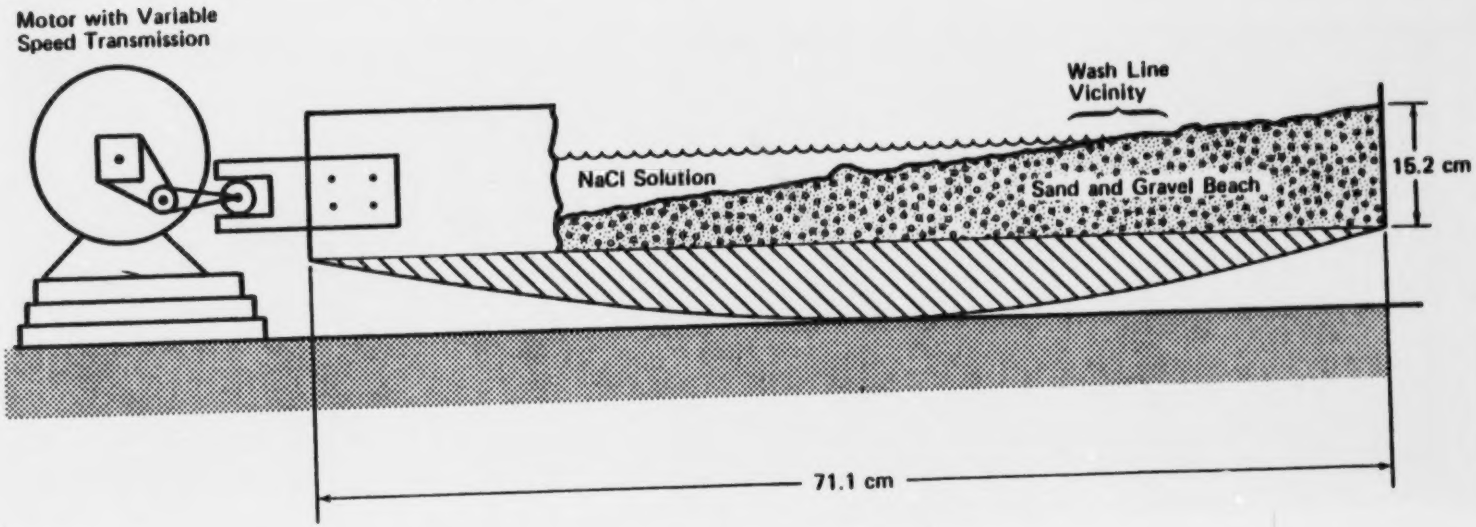

Motor with Variable Speed Transmission
Wash Line Vicinity
NaCl Solution
Sand and Gravel Beach
15.2 cm
71.1 cm

Figure B-1. Mock-beach design.

that depth. The blots were then examined under short-wavelength ultraviolet light. Under ultraviolet light, aromatic residues from the oil exhibit a characteristic fluorescence that can be photographed. The approximate depths of oil penetration was then determined.

Evaluation of each agent in the oil resistance test was based on the following criteria:

- If oil remaining on the surface of the agent could be washed away with a gentle water stream, the agent was classified as having good cleanability characteristics for that grade of oil.

- If the oil penetrated the agent throughout the beach (at two or more depths), the agent was considered unsuccessful.

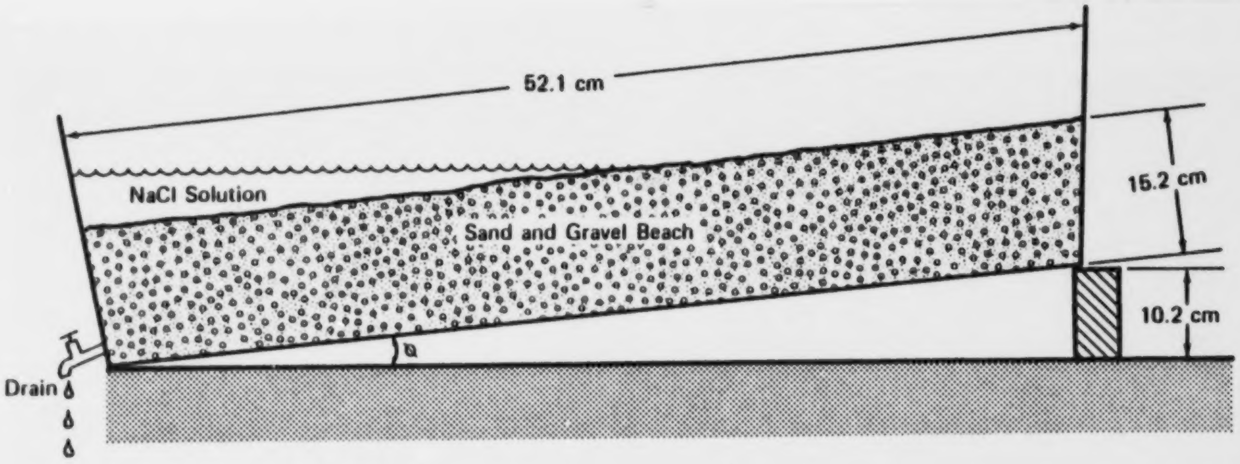
Test Procedures for Surfactants--
The surface collector was sprayed into the wash line of an oscillating mock beach. Dispersant A was sprayed over the surface of the mock beach.

Percolation Tests

The percolation test beach consisted of a circular container that was fitted with a bottom drain. The container, which was 52.1 cm in diameter and 25.4 cm deep, was inclined at an angle of approximately 11.5 degrees. Sand was placed in the test bed so that the surface was also inclined as shown in Figure B-2. The purpose of this construction was to simulate the seepage of water through a beach that occurs when a wave recedes from a high-water point. Testing was therefore done by carefully adding water to the top of the test bed and allowing the water to drain from the bottom.

A sand/gravel mixture was placed in the container to a depth of 15.2 cm. Synthetic sea water was then poured into the container until all the beach was submerged, allowing the beach material to settle. Water was then drained to a level below the beach surface. The beach material was replaced for each test.

The agents tested (Polyco 694, xanthan gum, and Amsco 3011) were then applied to the entire surface of each beach. Dry agents were sprinkled through a U.S. standard 200-mesh sieve, and solutions were sprayed. Post-treatment of the films (drying, heating, etc.) was then done, if necessary. Salt water was carefully introduced into the test beach from the top so that the film remained intact. Oil (#2, Kuwait, or #6) was then added, and the water was allowed to drain from the bottom, thus seeping through the beach. Water was introduced two additional times, allowing the previously applied oil either to float or to penetrate the film and beach. After three cycles, the beach was drained, sectioned, and examined for oil penetration at 1-inch intervals. Table B-3 gives the results of the percolation test for the selected agents.


52.1 cm
NaCl Solution
Sand and Gravel Beach
15.2 cm
10.2 cm
θ
Drain

$\theta \cong 11.5^{\circ}$

Surface Area ≅ 0.21 sq. meter

Figure B-2. Percolation test beach design.

TABLE B-3. PERCOLATION TEST

Agent, Concentration, Volume	Application	Conditions	Oil Added	Maximum Penetration	Comments
Polyco 694 2,346 ml/m^2 218 ml	Spray	Film dried	#2 fuel	Surface undercoating	Deep traces, probably from edge seepage
Xanthan gum 516.7 gm/m^2 48 gm	Dry powder	Misted with H_2O	#2 Fuel	Total penetration	Film appeared intact
Amsco 3011 2,346 ml/m^2 218 ml	Spray	Film dried	Kuwait crude	Surface undercoating	No oil found at depth

Other Tests

Tests were conducted on the mock beaches to determine the most economical application volume for the Amsco 3011. Beaches were sprayed with 3011 in volumes equivalent to 300 ml, 500 ml, and 600 ml over a surface area of 0.427 sq m. It was found that a 300-ml film was insufficient for effective coverage, but 500 ml or roughly 0.11 liter per 0.09 sq m produced an adequate film. It is important to note that a film of 3011 will not form if the beach is too wet. It therefore may be necessary in actual field applications to apply two light coatings of 3011. Both light coatings would dry more quickly than one heavy coating.

PRELIMINARY FIELD TESTS - SALT MARSHES

Surface treatment agents selected for the preliminary field tests are listed below:

1. Synthetic film-forming agent
    A. Polyvinyl acetate
2. Natural film-forming agents
    A. Xanthan gum
    B. Citrus pectin

3. Inorganic film-forming agents

    A. Sodium silicate

    B. Borate-silicate mixture

4. Surface collecting agent

5. Dispersing agents

    A. Agent A

    B. Agent B

    (Dispersant B, a hydrocarbon solvent-based dispersant, was added to the dispersing agent tests to determine if a hydrocarbon-based solvent dispersant behaves differently from the water-based dispersant, Agent A.)

A series of four laboratory tests was performed prior to the preliminary field tests to obtain qualitative and quantitative data on selected physical parameters that influence the application of these agents to stalks of cord grass (*Spartina foliosa*). Adherence to stalks, drying time, relative durability, and appearance were examined on wet and dry plants.

For the preliminary field tests, an outdoor test tank was constructed and placed at the preliminary field test site at Coyote Hills Slough in south San Francisco Bay. Marsh plots were placed in the tank, coated with each surface treatment agent, and tested to determine their resistance to contamination from an oil spill. Arabian crude oil, #2 fuel oil, and #6 fuel oil were used as the test oils. The effects of wave and tidal action and the ease of flushing were some of the parameters evaluated during the test tank simulation. Toxic effects of the surface treatment agents on the marsh plots was examined over a 6-month period.

Laboratory Tests

Experiment 1: Film-Forming Properties of Film-Forming Agents on Wet and Dry Specimens of *Spartina foliosa*--
Wet and dry stalks of *Spartina foliosa* were dipped in each of five film-forming agents - 0.5% and 1% xanthan gum; 0.5% and 1% citrus pectin; 1%, 2%, and 3% borate-silicate mixture; 1.90%, 2%, and 3% sodium-silicate and 100% polyvinyl acetate. Six stalk samples, three wet and three dry, were dipped in each agent at the above concentrations and placed on paper towels to dry. All samples, with the exception of the polyvinyl acetate, formed colorless films that were difficult, if not impossible, to detect visually. Use of a hand microscope did not enhance detection efficiency.

The xanthan-gum samples (0.5% and 1%) exhibited traces of film where the agent had accumulated, e.g., between the culm and leaves. In some instances the agent had not completely dried overnight. No samples of citrus pectin or sodium silicate produced visually detectable films.

The samples that were treated with the borate-silicate mixture (1% and 2%) showed some milky spots, denoting the presence of a partial film. The 3% solution revealed crystals on two plants, denoting poor film-forming capabilities.

The samples treated with polyvinyl acetate were almost completely covered by a white film. Little difference was noted between the wet and dry samples.

Experiment 2: Film-Forming Capabilities on Wet and Dry Surfaces of Cellulose Before Drying--

Small pieces of Spartina foliosa cellulose of approximately equal length and diameter were dipped in the agents enumerated in Experiment 1 and at the concentrations indicated. Three wet and three dried culm sections with the outer sheath removed were used as samples in this experiment for the agents and concentrations shown in Table B-4. Rhodamine-B dye was added to each agent before the dip test in order to enhance visual inspection of the film.

The presence of film was evaluated on a yes-no basis only. A film that appeared continuous or that covered at least 90% of the sample was given a "yes" response. Table B-4 presents the results of this experiment; xanthan gum and polyvinyl acetate produced the best films on both wet and dry surfaces. The 3% sodium silicate exhibited an almost complete film on the dry Spartina, and the 1% citrus-pectin film was about 90% complete on the wet Spartina.

Experiment 3: Film-Forming Capabilities on Wet and Dry Surfaces of Cellulose After Drying--

The agents applied to the culm sectins in Experiment 2 were allowed to dry for 2 hours. Each culm section was then visually inspected in both natural and ultraviolet light for the presence of a film. The results of this experiment are shown in Table B-5.

In general, the test results showed that the 3% solutions of the borate-silicate mixture and the sodium silicate formed very light films of almost 100% coverage on the wet surfaces and somewhat less on the dry surfaces. The ultraviolet light provided little assistance with these two agents. The xanthan-gum samples exhibited at least 75% film coverage for both wet and dry samples, although the wet samples appeared to be covered better.

The film formed by the citrus pectin was most complete on the wet surface. The ultraviolet light showed little evidence of film except for some areas where the agent had accumulated.

The polyvinyl acetate formed a 100% film on both the wet and dry surfaces from natural light observations, but the black light showed that the dry section had a less complete film than the wet.

Experiment 4: Simulated Wave and Tidal Action on Dry Agents--

The culm sections from Experiment 3 that were protected by dry agents were subsequently washed with water by a device that simulates wave and tidal

TABLE B-4. FILM-FORMING CAPABILITIES OF FILM-FORMING AGENTS ON DRY AND WET VEGETATIVE SURFACES, BEFORE DRYING

Agent	Dry Spartina	Wet Spartina	Notes
0.5% Xanthan gum	Yes	Yes	1% solution formed better overall film. 1% solution produced 100% coverage; 0.5% approximately 90%.
1.0% Xanthan gum	Yes	Yes	
0.5% Citrus pectin	No	No	1% solution formed better overall film. 1% solution on wet plants produced approximately 90% film coverage.
1.0% Citrus pectin	No	Yes	
1.0% Sodium silicate	No	No	3% solution formed best film on both wet and dry Spartina. Dry Spartina most amenable to film covering entire treated area.
2.0% Sodium silicate	No	No	
3.0% Sodium silicate	Yes	No	
1.0% Borate-silicate mixture	No	No	3% solution formed best film on both wet and dry Spartina. Films quite incomplete - up to 50% coverage of treated area
2.0% Borate-silicate mixture	No	No	
3.0% Borate-silicate mixture	No	No	
100% Polyvinyl acetate	Yes	Yes	Wet Spartina better covered than dry.

Note: Rhodamine-B dye was used to enhance visual inspection.

TABLE B-5. FILM-FORMING CAPABILITIES OF FILM-FORMING AGENTS ON WET AND DRY VEGETATIVE SURFACES, AFTER DRYING

Agent	Natural Light	Black Light
0.5% Xanthan gum	Wet: Light film approximately 100% complete Dry: Light film with heavier blotches, approximately 75% complete	Very difficult to see treated areas on both wet and dry plants; some areas of heavy concentration fluoresced well
1.0% Xanthan gum	Wet: Light film, approximately 100% complete with some heavier concentration Dry: Heavier film than wet plant; almost 100% complete	Heavy accumulations of agent were visible, but light film, if present, was difficult to detect
0.5% Citrus pectin	Wet: Very thin film, about 90% complete if scraped off Dry: Incomplete film	Little evidence of film present; some bright spots on both wet and dry plants where agent accumulated
1% Citrus pectin	Wet: Very thin film with some incomplete areas Dry: Incomplete film - approximately 50% coverage	Little evidence of film present; some bright patches on both wet and dry plants where agent accumulated
1% Sodium silicate	Wet: Very thin film with areas of no covdrage Dry: More incomplete than wet, splotchy appearance	Little evidence of film present
2% Sodium silicate	Wet: Very thin film with areas of no coverage Dry: More incomplete than wet; grainy appearance	Little evidence of film present
3% Sodium silicate	Wet: Very light film, almost 100% complete Dry: Less complete film than wet plant; blotchy appearance for both	Little evidence of film present; some bright patches
1% Borate-silicate mixture	Wet: Very light film with many areas not covered at all Dry: Film less uniform than wet; poor coverage	Little evidence of film present; some bright spots on both wet and dry plants
2% Borate-silicate mixture	Wet: Very light film with patches of no coverage Dry: Film less uniform than wet; poor coverage	Film noticeable but very incomplete (approximately 50%); better coverage on wet than on dry
3% Borate-silicate mixture	Wet: Light film with almost 100% coverage Dry: Not a complete film; poor coverage	Light film discernible on both wet and dry, almost complete on wet; some bright patches present
100% Polyvinyl acetate	Wet: 100% covered by a light film Dry: 100% covered by a light film	Very complete film - visible on wet plant; dry plant appeared to have 50% to 75% complete film

Note: Rhodomine-B dye used to enhance visual inspection in both natural and ultraviolet light.

action. The culm sections were washed for 5 minutes each. Each section was washed with 250 ml of water every 15 seconds during the 5-minute period. A schematic of the wave device is shown in Figure B-3. The results of this test are shown in Table B-6.

The xanthan-gum samples showed almost 100% removal of the agent for both wet and dry surfaces; only in areas where the agent had heavily accumulated did a residue remain. The citrus pectin appeared to maintain a thin film on the dried culm sections. The wet culm sections had almost 100% film removal.

The samples of the sodium-silicate and borate-silicate mixture had almost 100% film removal from the wet samples, while a slight residue remained on the dried samples. The 3% agent solutions left a very thin film on both the wet and dried plants.

The polyvinyl acetate was almost completely removed from both the wet and dry samples, although inspection under the ultraviolet light showed that a very light, continuous film was still visible on both the wet and dry samples. The ultraviolet light was used only on these samples because it did not enhance detection of the other agents in previous experiments.

Results—

In general, the films formed better on the wet cellulose sections than on the dry sections. This was observed both before and after the agent dried. The 3% sodium-silicate solution was something of an anomaly because it formed a better film on the dry cellulose sections. The best films overall were formed by the xanthan gum (1%) and the polyvinyl acetate. Generally, the highest concentration of the agent formed the best film. The use of Rhodamine-B dye and ultraviolet light enhanced film detection. The concentrations of each agent selected for the preliminary field tests were 1% xanthan gum, 1% citrus pectin, 3% sodium silicate and 3% borate-silicate mixture. The polyvinyl acetate was tested only at full strength. These concentrations were chosen on the basis of film-forming ability and durability under simulated wave and tidal action.

Field Tests

The preliminary field tests were carried out in a tank. Each test slot was separated by a barrier to prevent contamination of individual marsh sections by the agents applied. A 10-degree slope roughly simulated the slope of a salt marsh. A separate holding basin at the end of the tank retained the oil until a test was ready to be conducted. A wave generator, located in the rear of the tank, was hand-operated and deliverted 10.2- to 15.2-cm waves at the rate of about 60 per minute.

The basic test procedure for the citrus-pectin, xanthan-gum, sodium-silicate, borate-silicate mixture, and polyvinyl-acetate experiments is outlined below.

- Applying the film-forming agents to marsh sections, drying, and observing the tidal variation and wave action

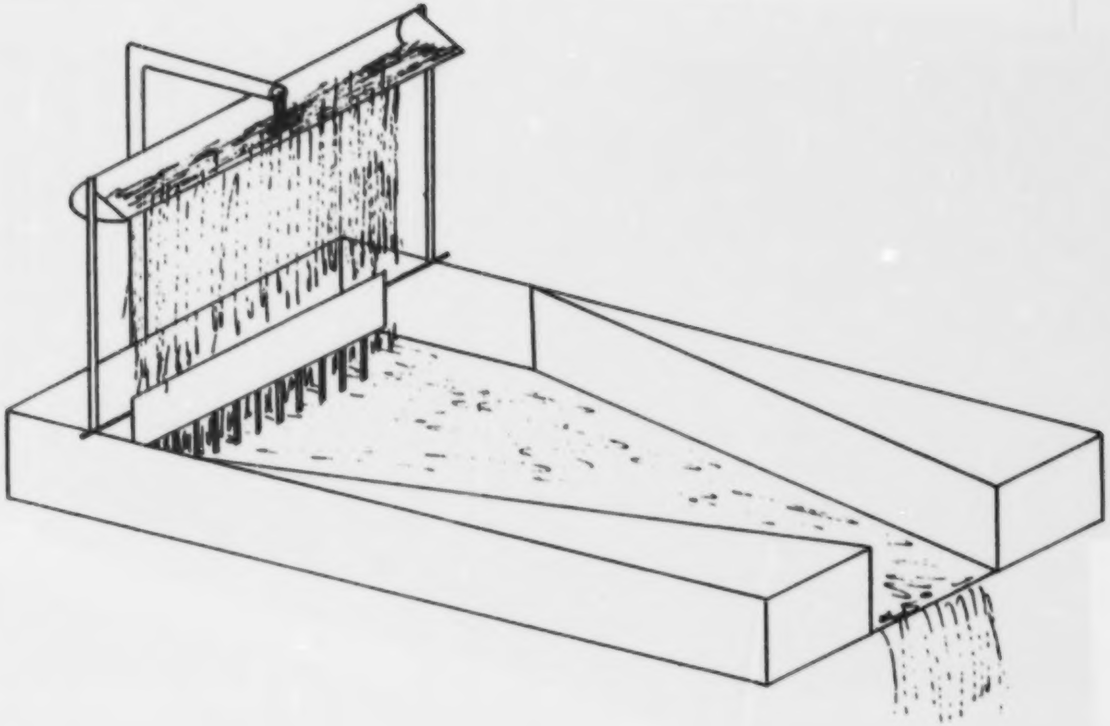


Figure B-3. Laboratory wave device.

TABLE B-6. FILM RETENTION AFTER SIMULATED WAVE AND TIDAL ACTION

Agent	Degree of Removal
0.5% Xanthan gum	Wet: Almost 100% removal of film Dry: Almost 100% removal of film
1% Xanthan gum	Wet: Almost 100% removal of film Dry: Areas where film was heaviest still contained some film after washing
0.5% Citrus pectin	Wet: 100% removal estimated Dry: Heavier concentration worked off, but thin film still remained
1% Citrus pectin	Wet: Almost 100% removal of film Dry: Not too discernibly affected by washing; thin film still remained
1% Sodium silicate	Wet: Almost 100% removal of film, although 2 of the 3 samples did show a slight film remaining Dry: Fairly uniform loss of almost all the film in all 3 samples
2% Sodium silicate	Wet: Almost 100% removal of film Dry: Very light residue noticeable on 2 samples
3% Sodium silicate	Wet: Very thin film still partially visible Dry: Slightly more film remained than on wet plant surface
1% Borate-silicate mixture	Wet: 100% removal estimated; very slight traces of film Dry: Almost 100% removal of film, although slightly more prominent traces than on wet surface
2% Borate-silicate mixture	Wet: Very light film still visible, although almost completely removed Dry: Little difference between wet and dry plants
3% Borate-silicate mixture	Wet: Very light film still visible Dry: Somewhat less removal of film than on the wet sample (average of the 3 samples)
100% Polyvinyl acetate	Wet: Film almost 100% removed, although slight film partially visible Dry: Slightly more film remained than on wet surface
100% Polyvinyl acetate*	Wet: Very thin film still visible and appeared continuous Dry: Thin film remained and appeared continuous

* Ultraviolet light observation.

* Applying the three reference oils to marsh sections without agents and observing the effects of tidal and wave action

* Applying the film-forming agents to marsh sections, drying, adding #2 fuel oil, simulating wave action, and flushing

* Applying the film-forming agents to marsh sections, drying, adding #6 fuel oil, simulating wave action, and flushing

* Applying the film-forming agents to marsh sections, drying, adding Arabian crude oil, simulating wave action, and flushing

Similar tests were conducted for the surfactants. However, a 5-minute drying time was allowed for the surface collector, while dispersant B and dispersant A were applied to the plants and to the water directly in front of the plants as the oil approached.

The tank was filled with approximately 500 gallons of sea water prior to each testing session. At each testing session, the salinity and water temperature were recorded, as well as the wind speed, air temperature, and relative humidity as shown in Tables B-7 through B-10.

Marsh sections of Spartina foliosa were removed from a nearby test plot. Sections were approximately 91.5 cm long by 30.5 cm wide and were trimmed at the bottom to a 15.2- to 20.3-cm thickness. This depth was judged to be sufficient to keep the major portion of the rhizomes or root system intact. Each marsh section was placed on a portable tray and carried to the tank for testing. Infrared photographs were taken of each marsh section at this point in order to document the plants in their natural state. Infrared photos were taken after each test in order to determine the efficacy of the agents in protecting the plants and the effects of the oil and agents. Eight agents were tested in all, each in conjunction with three different types of oil: #2 fuel oil, #6 fuel oil, and Arabian crude oil. The film-forming agents have been described previously and were used in concentrations that formed the best films in the laboratory testing. Each agent was applied by spraying, although the actual means varied slightly (see Tables B-11 through B-14). Application equipment is discussed in this appendix under Preliminary Field Tests - Beach Data. The volume and concentration of each agent were recorded and each agent applied evenly to the marsh plants and substrate. After application, with the exception of the surface collector, dispersant B and dispersant A, the agents were allowed to dry for up to 2 hours. The surface collector was allowed to dry for 5 minutes, but the dispersants were applied simultaneously to the marsh section and to the water immediately in fronont of the section as the oil approached the samples.

After the applied agents had dried, the trays were placed in the appropriate slot in the tank and submerged until approximately half the section was under water to simulate tidal action. This procedure allowed the oil to contaminate the plants that were partially submerged and those that remained above the waterline but were splashed by waves; it also allowed the oil to contaminate the substrate during the simulated wave action. In the initial tests the placement of the marsh sections allowed inspection of the

TABLE B-7. WEATHER AT TIME OF AGENT APPLICATION TO CONTROL MARSH PLOTS (no oil used)*

Agent Tested	Date	Temperature (^{o}C) Air	Temperature (^{o}C) Water	Wind Speed (km/hr)	Drying Time (min)
3% Sodium silicate	12 Jan 77	12	9	8.0	120
1% Xanthan gum	12 Jan 77	12	9	8.0	105
1% Citrus pectin	12 Jan 77	12	9	8.0	105
3% Borate-silicate mixture	12 Jan 77	12	9	8.0	90
100% Polyvinyl acetate	12 Jan 77	12	9	8.0	75
100% Surface collector	21 Jan 77	14	11	6.4	--
100% Dispersant B	21 Jan 77	14	11	6.4	--
2% Dispersant A	21 Jan 77	14	11	6.4	--

* Salinity - 32 ppt.

TABLE B-8. WEATHER AT TIME OF AGENT APPLICATION TO MARSH PLOTS CONTAMINATED BY #2 FUEL OIL*

Agent Tested	Date	Temperature (^{o}C)		Wind Speed (km/hr)	Humidity (%)	Drying Time (min)
		Air	Water			
1% Citrus pectin	13 Jan 77	10.0	7	3-5	80	90
3% Borate-silicate mixture	13 Jan 77	10.0	7	3-5	80	
3% Sodium silicate	13 Jan 77	10.0	7	3-5	80	90
1% Xanthan gum	13 Jan 77	10.0	7	3-5	80	
100% Polyvinyl acetate	13 Jan 77	10.0	7	3-5	80	
Control section	13 Jan 77	10.0	7	3-5	80	90
100% Surface collector	21 Jan 77	14	11	8.0	75	
100% Dispersant B	21 Jan 77	14	11	8.0	75	
2% Dispersant A	21 Jan 77	14	11	8.0	75	--

* Salinity - 32 ppt.

TABLE B-9. WEATHER AT TIME OF AGENT APPLICATION TO MARSH PLOTS CONTAMINATED BY ARABIAN CRUDE OIL*

Agent Tested	Date	Temperature (°C) Air	Temperature (°C) Water	Wind Speed (km/hr)	Humidity (%)	Drying Time (min)
3% Sodium silicate	14 Jan 77	16	9	8.0	75	120
1% Citrus pectin	14 Jan 77	16	9	8.0	75	120
1% Xanthan gum	14 Jan 77	16	9	8.0	75	
3% Borate-silicate mixture	14 Jan 77	16	9	8.0	75	
100% Polyvinyl acetate	14 Jan 77	16	9	8.0	75	
Control section	14 Jan 77	16	9	8.0	75	--
100% Polyvinyl acetate	18 Jan 77	--	--	5.0	85	
Control section	18 Jan 77	--	--	--	--	--
2% Dispersant A	19 Jan 77	17	6	5.0	85	
100% Dispersant B	19 Jan 77	17	6	5.0	85	
1% Xanthan gum	20 Jan 77	17	8	3.0	85	
100% Polyvinyl acetate	20 Jan 77	17	8	3.0	85	
Control section	20 Jan 77	17	8	3.0	85	--
100% Surface collector	20 Jan 77	14	7	8.0	80	
100% Dispersant B	20 Jan 77	14	7	8.0	80	
2% Dispersant A	20 Jan 77	14	7	8.0	80	

* Salinity - 32 ppt.

TABLE B-10. WEATHER AT TIME OF AGENT APPLICATION TO MARSH PLOTS CONTAMINATED BY #6 FUEL OIL*

Agent Tested	Date	Temperature (^{o}C)		Wind Speed (km/hr)	Humidity (%)	Drying Time (min)
		Air	Water			
1% Xanthan gum	17 Jan 77	17	10.0	6.4-8.0	70	
3% Sodium silicate	17 Jan 77	17	10.0	6.4-8.0	70	90
3% Borate-silicate mixture	17 Jan 77	17	10.0	6.4-8.0	70	
1% Citrus pectin	17 Jan 77	17	10.0	6.4-8.0	70	75
100% Polyvinyl acetate	17 Jan 77	17	10.0	6.4-8.0	70	
Control section	17 Jan 77	17	10.0	6.4-8.0	70	--
100% Surface collector	21 Jan 77	14	11.0	8.0	75	
100% Dispersant B	21 Jan 77	14	11.0	8.0	75	
2% Dispersant A	21 Jan 77	14	11.0	8.0	75	

* Salinity - 32 ppt.

TABLE B-11. CONTROL MARSH PLOTS TEST DATA
(no oil used)

Agent Tested	Plant Appearance	Agent Durability	Volume of Agent (ml)	Notes
3% Sodium silicate	Thin film on plant (dry) but moist surface	Poor - no film visible	500	Wave action only (10 min), garden sprayer on dry plants
1% Xanthan gum	Plant and surface still wet	Good - jellylike surface on soil	1000	Wave action only (10 min), garden sprayer on dry plants
1% Citrus pectin	Thin film on plant (dry) but moist surface	Poor - no film visible	750	Wave action only (10 min), garden sprayer on dry plants
3% Borate-silicate mixture	Thin film on plant (dry) but moist surface	Poor - no film visible	450	Wave action only (10 min), garden sprayer on dry plants
100% Polyvinyl acetate	Film-covered (dry) on both plant and surface	Excellent - good cover	150	Wave action only (10 Min), spray gun on dry plants
3% Sodium silicate	Thin film on plant (dry) but moist surface	Poor - no film visible	500	Tidal action only (15 min), garden sprayer on wet plants
1% Xanthan gum	Plant and surface still wet	Good - jellylike surface on soil	1000	Tidal action only (15 min), garden sprayer on wet plants
1% Citrus pectin	Thin film on plant (dry) but moist surface	Poor - no film visible	750	Tidal action only (15 min), garden sprayer on wet plants
3% Borate-silicate mixture	Both plant and surface still wet	Poor - no film visible	450	Tidal action only (15 min), garden sprayer on wet plants
100% Polyvinyl acetate	Not quite as good as when wet, but still good	Excellent - good cover	150	Tidal action only (15 min), spray gun on wet plants
100% Surface collector	Generally thin film on both plants and soil	--	30	Garden spray
100% Dispersant B	Generally thin film on both plants and soil	--	50	Spray gun
2% Dispersant A	Generally thin film on both plants and soil	--	500	Garden spray

B-12

TABLE B-12. MARSH PLOTS CONTAMINATED BY #2 FUEL OIL - TEST DATA

Agent Tested	Plant Appearance	Substrate Penetration by Oil	Agent Durability	Ease of Flushing Oil with Water Spray	Volume of Agent (ml)	Notes
1% Citrus pectin	Oily sheen on plants	Very little	Poor	Fair*	500	7-minute wave action, sprayed on plants and soil, garden spray
3% Borate-silicate mixture	Oily sheen on plants	Very little	Poor	Fair*	500	7-minute wave action, sprayed on plants and soil, garden spray
3% Sodium silicate	Oily sheen on plants	Very little	Poor	Fair*	450	7-minute wave action, sprayed on plants and soil, garden spray
1% Xanthan gum	Light oil sheen on plants	Very little	Good	Fair*	500	7-minute wave action, sprayed on plants and soil, garden spray
100% Polyvinyl acetate	Light oil sheen on plants	Very little	Excellent	Fair*	150	7-minute wave action, sprayed on plants and soil, garden spray
Control section	Heavy oil sheen	Very little	--	Fair*	--	7-minute wave action
100% Surface collector	Light oil sheen on plants	Very little	--	Good - small droplets were formed by agent and were easy to wash off	50	8-minute wave action, sprayed on plants and soil, hand sprayer
100% Dispersant B	Light oil sheen on plants	Very little	--	Good - the oil was dispersed to some extent before reaching plants	65	8-minute wave action, sprayed in front of oil, spray gun
2% Dispersant A	Light oil sheen on plants	Very little	--	Good - the oil was dispersed to some extent before reaching plants	500	8-minute wave action, sprayed in front of oil, hand sprayer

* #2 fuel oil, being a light hydrocarbon, seems to be flushed fairly easily from the plants. It is very difficult, however, to note oil penetration into the plant leaf cells. The visibility of oil on the plants is limited. In the control plot and the 1% citrus-pectin plot, the oil contaminated the plants nearest the water line, the mud on both sides, and the back of the test plot.

B-13

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TABLE B-13. MARSH PLOTS CONTAMINATED BY ARABIAN CRUDE OIL - TEST DATA

Agent Tested	Plant Appearance	Substrate Penetration by Oil	Agent Durability	Ease of Flushing Oil with Water Spray	Volume of Agent (ml)	Notes
3% Sodium silicate	Heavy oily layer on plants and soil	Very little	Poor	Fair - similar to control plot	500	7-minute wave action, sprayed on plants and soil, garden spray
1% Citrus pectin	Heavy oil layer on plants and soil	Very little	Poor	Fair - similar to control plot	500	7-minute wave action, sprayed on plants and soil, garden spray
1% Xanthan gum	Heavy oil layer on soil but less on plants	Very little	Good	Good - the jelly-like layer helps the flushing to a degree	500	7-minute wave action, sprayed on plants and soil, garden spray
3% Borate-silicate mixture	Very heavy oil on plants and soil	Very little	Poor	Fair - similar to control plot	500	7-minute wave action, sprayed on plants and soil, garden spray
100% Polyvinyl acetate	A little less oil on plants than on control	Very little	Excellent	Very good - although some was fairly clean	150	7-minute wave action, sprayed on plants and soil, garden spray
Control section	Heavy oily layer	Very little	--	Fair - flushing seemed to remove over 50% of the oil	--	7-minute wave action
2% Dispersant A	Heavy oily layer on soil and plants	Very little	--	Fair - similar to control plot	500	10-minute wave action, sprayed on plant; however, this method not recommended; garden spray
100% Dispersant B	Moderate oil layer on plants and soil	Very little	--	Very good - the oil seemed to be emulsified by the surfactant	100	10-minute wave action, sprayed on plant; however, this method not recommended; spray gun
1% Xanthan gum	Heavy oil layer on soil but less on plants	Very little	Good	Good - the jelly-like layer helps the flushing to a degree	1000	7-minute wave action, sprayed on plants and soil, hydraulic spray
100% Polyvinyl acetate	A little less on plants thn on control	Very little	Excellent	Very good - although some was fairly clean	200	7-minute wave action, sprayed on plants and soil, hydraulic spray
Control section	Heavy oil layer	Very little	--	Fair - flushing seemed to remove over 50% of the oil	--	7-minute wave action
100% Surface collector	Little oil on plants and soil	Very little	--	Very good - oil formed small droplets that were easily washed off	30-50	7-minute wave action, sprayed on plants and soil, spray gun
100% Dispersant B	Some oil on surface but little on plant	Very little	--	Very good - oil was emulsified and easy to remove by flushing	75	7-minute wave action, sprayed in front of oil, spray gun
2% Dispersant A	Little oil on plants and soil	Very little	--	Very good - oil was emulsified and easy to remove by flushing	500	7-minute wave action, sprayed in front of oil, garden sprayer

TABLE B-14. MARSH PLOTS CONTAMINATED BY #6 FUEL OIL - TEST DATA

Agent Tested	Plant Appearance	Substrate Penetration by Oil	Agent Durability	Ease of Flushing Oil with Water Spray	Volume of Agent (ml)	Notes
1% Xanthan gum	Heavy oil layer on plants and soil	Very little	Good	Fair - oil did flush from soil	500	7 minutes of wave action, sprayed on soil and plants, garden sprayer
3% Sodium silicate	Heavy oil layer on plants and soil	Very little	Poor	Poor - little to no oil flushed	500	7 minutes of wave action, sprayed on soil and plants, garden sprayer
3% Borate-silicate mixture	Heavy oil layer on plants and soil	Very little	Poor	Poor - little to no oil flushed	500	7 minutes of wave action, sprayed on soil and plants, garden sprayer
1% Citrus pectin	Heavy oil layer	Very little	Poor	Poor - little to no oil flushed	500	7 minutes of wave action, sprayed on soil and plants, garden sprayer
100% Polyvinyl acetate	Heavy oil layer on plants and soil	Very little	Excellent	Fair - little did flush from soil	200	7 minutes of wave action, sprayed on soil and plants, garden sprayer
Control section	Heavy oil layer on plants and soil	Very little	--	Poor - little to no oil flushed	--	7 minutes of wave action
100% Surface collector	Moderate oil layer on plants	Very little	--	Good - oil flushed fairly well from plants but not as well from soil	50	7 minutes of wave action, sprayed on soil and plants, garden sprayer
100% Dispersant B	Heavy oil layer on plants and soil	Very little	--	Poor - little to no oil flushed	65	7 minutes of wave action, sprayed in front of oil, spray gun
2% Dispersant A	Heavy oil layer on plants and soil	Very little	--	Fair - oil did not flush from plants but a little did flush from soil	500	7 minutes of wave action, sprayed in front of oil, spray gun

relative degree of removal of each agent by tidal and wave action. In testing the control sections in which the agent was applied without oil, Rhodamine-B dye and food coloring were used to facilitate the determination of the relative durability of each agent on cellulose. These results were compared with the laboratory evaluation results.

For those tests involving oil, a holding basin was used to retain the oil behind a movable dam. This allowed the oil to spread quite evenly over the water surface, subjecting each marsh section to approximately equal volumes of oil. The volume of oil used in each test varied with the oil being tested. For the #6 fuel oil test, 6 liters were used; for the Arabian crude oil test, 4 liters; and for the #2 fuel oil test, 2 liters. This difference in volume was due to the relative viscosity of each oil and its ability to form a uniform film on the water. At the beginning of each test with oil, the dam was lifted and the oil "waved" into the vegetation for 5 to 7 minutes with a wave generator located at the end of the tank. Each wave was approximately 10.2 cm high, and the waves were produced at a rate of about 60 per minute. This frequency and time allowed the oil to move toward and contaminate each marsh section to the maximum extent possible with the volume of oil used. Each tray was then pulled out of the tank, and the marsh sections were observed visually for oil coverage, section appearance, and agent durability.

After the tray was removed from the test tank, each marsh section was flushed by a low-pressure water spray in order to estimate the ease of flushing of the oil from the plants and their substrate. Infrared photos were then taken of each marsh section to provide a comparison with the photos taken prior to agent application or oil contamination. Oil penetration into the substrate was checked by ultraviolet light after flushing by removing a section of the oiled substrate. The fluorescent properties of the oil could be distinguished from the fluorescence caused by some of the agents, thereby determining the penetration of the oil. Since #6 fuel oil does not fluoresce, no penetration data were directly obtained for this oil, but the viscosity of the oil is such that actual penetration would be negligible.

After each test the marsh sections were returned to their original plots and marked for future observation. Oil was removed from the tank by use of sorbent pads and steam cleaning. Any contaminated oil/water mixture was run through a separator and embiber beads to remove the last traces of oil. Uncontaminated water was returned to a nearby slough.

The entire test site was cleaned and policed after all testing was concluded. All debris was disposed of in accordance with recommended procedures.

Results

Unoiled Control Plots--

Surface treatment agents were sprayed onto both wet and dry Spartina without any oil being used. In both cases, the marsh soil was moist. The environmental conditions at the time of agent application and their drying times are given in Table B-7. A summary of the control marsh-plot tests is given in Table B-11.

After being sprayed on dry plants and over a period of 1 to 2 hours, the citrus pectin, sodium silicate, borate-silicate mixture, and polyvinyl acetate all formed a dry film on the dry plants. The xanthan gum, however, retained a jellylike consistency on both the plants and substrate. The surface collector and dispersant B, each having an organic base, formed an oily film on the plants and soil. Except for polyvinyl acetate, which formed a rubbery crust on the soil, all agents remained moist on the marsh soil as a result of the retained moisture in the marsh mud.

Xanthan gum, citrus pectin, sodium silicate, borate-silicate mixture, and polyvinyl acetate were tested to determine their durability under simulated wave action for 10 minutes. After this time no film was visible on the soil or plants sprayed with citrus pectin, sodium silicate, or borate-silicate mixture. A thick film of xanthan gum was still visible on the marsh soil, but little was observed on the vegetation in the surf zone. Polyvinyl acetate, however, maintained an excellent film on the soil and a very good film on the plants after the simulated wave action. A week later, polyvinyl acetate remained on the marsh soil, although approximately 50% had dissolved or eroded away.

The same concentrations and volumes of sodium silicate, xanthan gum, citrus pectin, borate-silicate mixture, and polyvinyl acetate were sprayed on wet plants to determine their durability under tidal action. Sodium silicate, citrus pectin, borate-silicate mixture, and polyvinyl acetate were almost dry after 1 to 2 hours on the plants. Otherwise, no difference was observed between the agents sprayed on wet or dry marsh plants.

The agents were then tested under simulated tidal action by being submersed in sea water for 15 minutes. After this time, no film was visible for sodium silicate, citrus pectin, or borate-silicate mixture. The xanthan-gum film was observed on the soil but not on the plants. Polyvinyl acetate maintained an excellent film on the soil cover and a very good film on the marsh plants.

Plots Tested With #2 Fuel Oil--

Surface treatment agents were applied to eight marsh plots. An untreated marsh section was used as a control plot. All of the agents except for the surface collector, dispersant B, and dispersant A, were allowed to dry for approximately 1-1/2 hours before being tested. The environmental conditions at time of agent application and their drying times are shown in Table B-8. The test results are shown in Table B-12.

The #2 fuel oil was very difficult to observe on the plants. However, careful observation could detect contaminated plants by a shiny appearance or sheen on the leaves. A moderate oil sheen was noted on the citrus-pectin, sodium-silicate, borate-silicate mixture, and control marsh sections. Only a very light oil sheen was observed on the sections sprayed with polyvinyl acetate, xanthan gum, the surface collector, dispersant B, and dispersant A. It was very difficult to determine if the sheen on the surface collector or the dispersant B sections was due to the agent or the oil because both agents are hydrocarbon-based.

Citrus pectin, sodium silicate, and borate-silicate mixture exhibited poor durability during this test. Polyvinyl acetate was the most durable agent; xanthan gum, the surface collector, dispersant B, and dispersant A had good durability. The durability of the surface collector, dispersant B, and dispersant A relates both to the protective layer that remained on the plants and substrate and to the ability of these agents to break up the oil film before it reached the marsh section.

Substrate penetration by the oil, determined by using an ultraviolet light on cores, was found to be slight on all marsh sections, including the control. This may be because this test was conducted shortly after oiling and the oil did not have a chance to penetrate, or because the substrate itself acted as an efficient barrier.

The marsh sections were sprayed with a low-pressure water spray to determine the ease of flushing the oil from the plants and soil. Little, if any, difference in oil removal was observed between the control section and the sections protected by citrus pectin, borate-silicate mixture, and sodium silicate. The sections sprayed with xanthan gum and polyvinyl acetate had less of a sheen after flushing. This could indicate that the oil was removed from these sections by flushing or that the oil did not adhere to the vegetation. The sections protected by Shell Oil Herder caused the oil to form small droplets, which were easily washed from the plants and substrate by the water spray. The sections treated with dispersant B and dispersant A were easily cleaned by water spray. Only slight contamination was still noticeable after flushing.

Plots Tested With Arabian Crude Oil--

Surface treatment agents were applied to marsh plots. An untreated marsh section was used as a control plot. Some agents were tested more than once with Arabian crude oil because they were used for demonstration purposes. All agents except dispersant B, the surface collector, and dispersant A were allowed to dry for up to 2 hours before testing with oil. The environmental conditions at the time of agent application and their drying times are shown in Table B-9. The results of this phase are shown in Table B-13.

The test for agent durability was subjective and consisted of visually observing the agent film before and after wave and tidal action. In most cases the oil film covered the plant and soil, and deductions were made on the basis of laboratory experiments. The most persistent agent was the polyvinyl acetate. Once this agent had cured, it formed a rather solid protective surface. The xanthan gum was more persistent on the substrate than on the plants, thereby affording protection against significant oil penetration. The surface collector, dispersant A, and dispersant B results on agent durability were somewhat inconclusive because their manner of application differed from the other five agents. However, based on the light oiling observed, it was assumed that the agents had persisted quite well. It should be noted that for surfactants, durability relates both to the protective layer that remained on the plants and substrate and to the ability of these agents to break up the oil before it reached the marsh section.

Most of the marsh sections were quite heavily oiled upon removal from the test tank. The oil appeared to adhere to the plants and substrate despite the presence of the agents, i.e., there was little difference from the control section. The exceptions to this were the surface collector, dispersant B, and dispersant A. The method of application and the nature of the surfactants kept the oiling of the marsh section to a minimum. There was generally somewhat less oil on both the vegetation and substrate of the sections treated with polyvinyl acetate than on the control section.

Ease of flushing was tested using a low-pressure water spray. The easiest to flush were sections treated with polyvinyl acetate, the surface collector, dispersant A, and dispersant B. The others were not much different from the control, although the jellylike consistency of the xanthan gum did help somewhat in flushing the oil from the substrate. Oil on the polyvinyl-acetate-treated sections, especially the substrate, flushed easily; some oil traces were left on the plants. The surface collector caused formation of small oil droplets that were easily flushed from the plants and substrate. In the case of dispersant A and dispersant B, the oil was somewhat emulsified, which made its removal by flushing quite easy.

Substrate penetration by oil was determined by cutting a portion of the oiled substrate away from the marsh section and observing it under ultraviolet light. Since some of the agents fluoresce, it was necessary to carefully distinguish the agent from the oil when looking for oil on the surface and in the soil column. However, even though different volumes of oil and agent were observed on the surface of the samples, little or no penetration was observed in any of the marsh sections, including the control sections.

Plots Tested With #6 Fuel Oil--

Surface treatment agents were applied to eight marsh plots. An untreated marsh section was used as a control plot. Each agent, except the surface collector, dispersant B, and dispersant A, was allowed to dry between 1-1/4 and 2 hours before testing with oil. The environmental conditions at time of agent application and their drying times are shown in Table B-10. Test results are shown in Table B-14.

Except for the citrus pectin, sodium silicate, and borate-silicate mixture, all of the agents showed some durability during simulated wave action. Polyvinyl acetate was the most durable agent. Xanthan gum and the surface collector were also good. Dispersant B and dispersant A showed fair durability. It should be noted that for the surface collector, dispersant B, and dispersant A, durability relates both to the protective layer that remained on the plants and substrate and to the ability of these agents to break up the oil film before it reached the marsh section.

All marsh sections, except the section treated with the surface collector, had a thick layer of #6 fuel oil on the vegetation and substrate after simulated wave action. The surface collector tended to bead the oil into thick, round globules; this resulted in less contamination than with the other agents.

Little difference was observed between low-pressure water flushing of the control section and citrus pectin, sodium silicate, borate-silicate mixture, and dispersant B. Xanthan gum and polyvinyl acetate exhibited somewhat better results when flushing oil from the substrate, and the dispersant A flushed oil from the plants the most easily. The surface collector seemed superior to all the other agents in aiding the flushing of oil from the plants. It was also superior, but to a lesser extent, in aiding flushing of oil from the substrate.

Substrate penetration by the #6 fuel oil was not observed in any of the marsh sections tested, including the control. The high viscosity of the oil prevented penetration from occurring.

Results--

All of the film-forming agents formed a film on the dry cordgrass (Spartina foliosa), although not all films were complete. The effectiveness of the film-forming agents in protecting wet cordgrass and marsh soil from oil contamination varied significantly. Only xanthan gum and polyvinyl acetate formed a reasonable, effective, and long-lasting film over the cordgrass and marsh soil. It was recommended that xanthan gum and polyvinyl acetate be tested during the full-scale field tests to fully evaluate their effectiveness. The surfactants tested showed promise in preventing contamination of salt marshes by oil.

Toxicity of Agents to Marsh Plants

Test Procedures--

Toxicity tests were performed on 47 plots of cordgrass, (Spartina foliosa), which were growing adjacent to San Francisco Bay near the mouth of Coyote Hills Slough in Fremont, California. Each sample was removed from the ground with a plug of marsh soil measuring approximately one-third meter in width by one meter in length. A few of the plugs were cut in half to provide the requisite number of samples from the limited amount of test material. Care was taken to remove enough soil so that damage to roots and rhizomes was minimized.

Each plug was set in a specially constructed test tank at an angle to the horizontal in order to simulate the slope of a marsh surface into an adjacent body of water. Surface treatment agents and test oils were applied to each plot, as summarized in Table B-15, and wave action was simulated. The plots were then replaced in their original locations in the marsh for subsequent periodic examination. The location of each plot is shown in Figure B-4.

Data Collection--

Two types of data were collected throughout the sampling period:

* Each plot was qualitatively assessed for relative health and density of plants.

* Measurements were taken of the height of selected plants in each plot.

Initially, the turgor and color of the marsh grass provided adequate

TABLE B-15. SURFACE TREATMENT AGENTS, TEST OILS, AND MARSH TEST PLOTS*

Agent	Dry Control	Dry Control	#2 Fuel Oil	Arabian Oil	#6 Fuel Oil
3% Sodium Silicate	1	6	13	17	24
1% Xanthan gum	2	7	14	19 33	23
1% Citrus pectin	3	8	11	18	26
3% Borate-silicate mixture	4	9	12	20	25
100% Polyvinyl acetate	5	10	15	21	27 29 34
Surface collector	39	--	42	36	45
Dispersant B	40	--	43	32 37	46
Dispersant A	41	--	44	31 38	47
Control	--	--	16	22 30 35	28

* Entries signify plot numbers; see Figure B-1 for location of test plots.

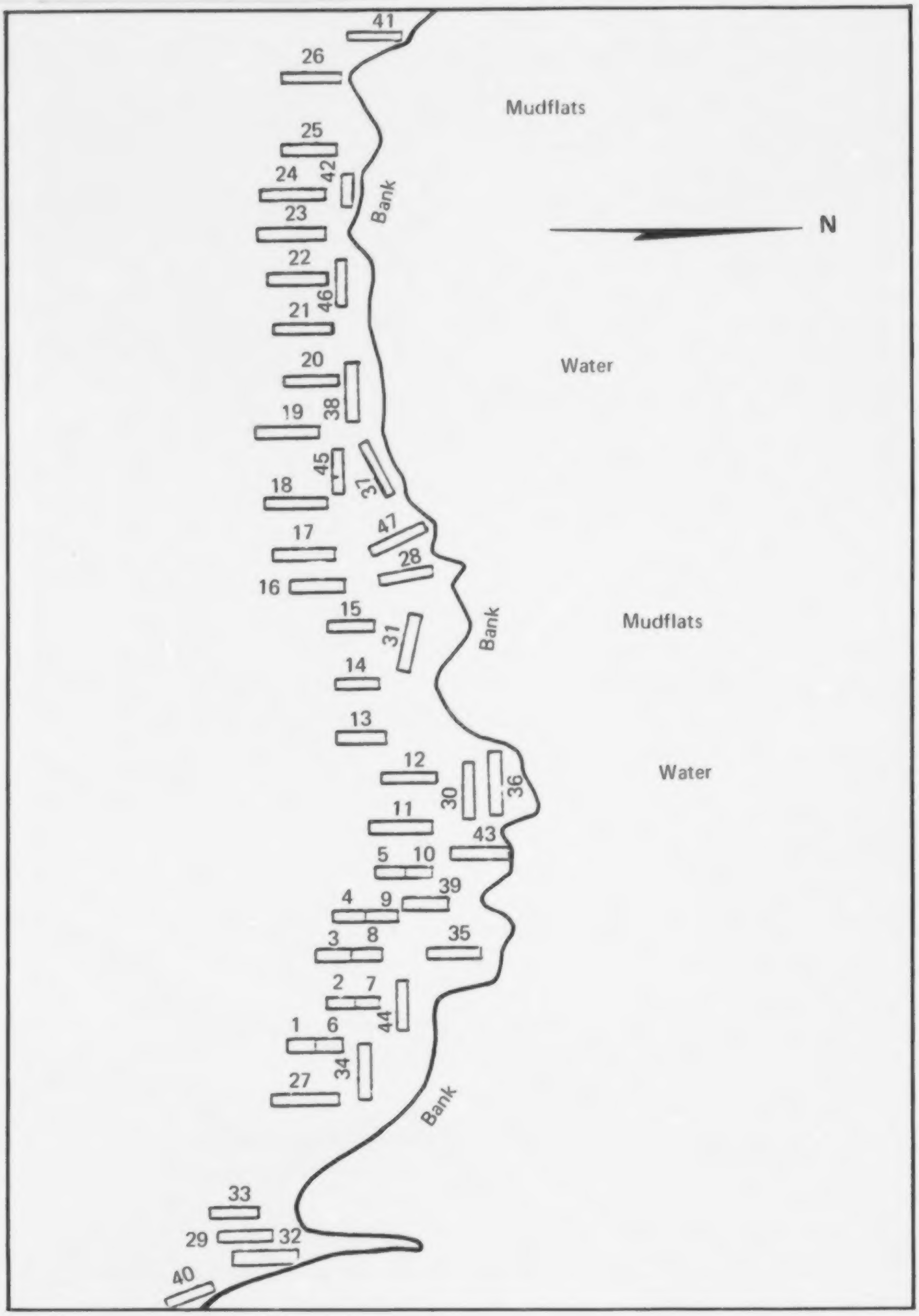

41
26
Mudflats
25
24
42
Bank
23
N
22
46
21
20
Water
38
19
45
37
18
17
47
28
16
15
31
Bank
Mudflats
14
13
12
30
36
Water
11
43
5
10
39
4
9
3
8
35
2
7
44
1
6
34
27
Bank
33
29
32
40

Figure B-4. Location of marsh test plots.

qualitative indicators of health. Healthy plants had resilient, green stems and leaves, and flaccid, brown stems typified unhealthy or dead plants. The relative density of the stems was also noted. Semiquantitative records were kept of each of these characteristics and were summed to provide an overall index of the health of each plot.

As time progressed, it became necessary to change the method of qualitative evaluation. Differences were no longer apparent in color or turgor of stems and leaves. Stem density remained the single semiquantitative index of each plot's health.

Height measurements were initiated when it became clear that the new (1977) growing season was underway. Ten individual plants, distributed along the central axis of each plot at intervals approximately equal to one-tenth the length of the plot, were tagged for continued observation. The tags consisted of grey duct tape attached to one end of a twisted loop of wire that loosely encircled the stem. One untwisted end of the wire was inserted into the marsh soil. The tags were difficult to maintain during the study period, and some tags were lost. It was necessary to resample the plants each time height measurements were taken. Records were kept on those plants whose tags were not lost but were considered insufficient for meaningful data analysis.

In keeping with the objectives of this study, the observations contained in this report should be considered only as initial indicators of the potential harm or benefit to be derived from the use of a given film-forming or other agent.

Qualitative Data--

Relative comparisons of plant reaction (e.g., health) to various treatments were made on the basis of qualitative observations. These comparisons are presented in Table B-16. In the first observation period, various degrees of plant mortality were observed in some test plots. These mortalities are shown in Table B-16 and were incorporated into the relative comparisons. While by no means conclusive, the distribution of lethal effects suggests possible agent toxicity in the concentrations used, possible oil/agent synergistic effects, or incomplete protection by the agent. Subsequent recovery of most plots where plant mortality was observed further suggests that the root and rhizome masses survived the treatment and that the "mortality" was only an aerial expression. No toxic responses to the film-forming agents were observed in the agent-treated control plots.

In general, most plots had recovered to approximately normal appearance by the final sampling period. A notable exception applies to some of the plots that were contaminated with #2 fuel oil. The control plot (no surface treatment agent applied) exposed to this oil remained very scantily vegetated throughout the sampling period. In contract, the plots that were very heavily oiled with #6 fuel oil remained in relatively good condition throughout the sampling period. Except for the portions of leaves and stems that were heavily oil-encrusted, the plants appeared to be healthy. It seems, then, that the oil that contains the greatest proportion of low-boiling fractions is most toxic to the marsh grass, whereas the heavier oil's impacts are physical in nature. (This is consistent with the observations of Jennifer M. Baker,

TABLE B-16. RELATIVE CONDITION OF PLANT HEALTH VS. TIME: QUALITATIVE OBSERVATIONS

	February 10	March 22	April 7	May 11	June 23
1.*	Sodium silicate **	Sodium silicate	Sodium silicate	No observable difference	Sodium silicate
2.	Xanthan gum	Xanthan gum	Borate silicate		Xanthan gum
3.	Polyvinyl acetate	Citrus pectin	Surface collector		Citrus pectin
4.	Citrus pectin	Surface collector	Xanthan gum		Borate silicate
5.	Borate silicate	Dispersant B	Dispersant A		Polyvinyl acetate
6.	Surface collector	Dispersant A	Polyvinyl acetate		Surface collector
7.	Dispersant B	Borate silicate	Citrus pectin		Dispersant A
8.	Dispersant A	Polyvinyl acetate	Dispersant B		Dispersant B
1.	Sodium silicate	Citrus pectin	Polyvinyl acetate	No observable difference	No observable difference
2.	Borate silicate	Sodium silicate	Sodium silicate		
3.	Polyvinyl acetate	Xanthan gum	Citrus pectin		
4.	Citrus pectin	Polyvinyl acetate	Borate Silicate		
5.	Xanthan gum	Borate silicate	Xanthan gum		
1.	Sodium silicate	Sodium silicate	Sodium silicate	Sodium silicate	Sodium silicate
2.	Borate silicate	Dispersant A	Dispersant A	Xanthan gum	Xanthan gum
3.	Polyvinyl acetate	Dispersant B	Surface collector	Citrus pectin	Citrus pectin
4.	Dispersant B	Surface collector	Xanthan gum	Polyvinyl acetate	Polyvinyl acetate
5.	#Citrus pectin	Polyvinyl acetate	Dispersant B	Surface collector	Surface collector
6.	#Control	Citrus pectin	Citrus pectin	Dispersant B	Dispersant B
7.	Surface collector	Borate silicate	Polyvinyl acetate	Dispersant A	Dispersant A
8.	Dispersant a	Xanthan gum	Borate silicate	Borate silicate	Borate silicate
9.	#Xanthan gum	Control	Control	Control	Control
1.	Sodium silicate	Borate silicate	Borate silicate	No observable difference	Sodium silicate
2.	Control	Xanthan gum	Sodium silicate		Xanthan gum
3.	Borate silicate	Sodium silicate	Citrus pectin		Citrus pectin
4.	Xanthan gum	Citrus pectin	Xanthan gum		Borate silicate
5.	Polyvinyl acetate	Surface collector	Polyvinyl acetate		Polyvinyl acetate
6.	Dispersant B	Dispersant A	Dispersant A		Dispersant B
7.	#Citrus pectin	Polyvinyl acetate	Control		Dispersant A
8.	Dispersant A	Control	Dispersant B		Control
9.	#Surface collector	Dispersant B	Surface collector		Surface collector
1.	Xanthan gum	Sodium silicate	Surface collector	Sodium silicate	No observable difference
2.	Citrus pectin	Citrus pectin	Xanthan gum	Xanthan gum	
3.	Polyvinyl acetate	Polyvinyl acetate	Borate silicate	Citrus pectin	
4.	Borate silicate	Surface collector	Dispersant B	Borate silicate	
5.	Dispersant B	Dispersant B	Dispersant A	Polyvinyl acetate	
6.	Sodium silicate	Xanthan gum	Control	Control	
7.	#Surface collector	Dispersant A	Sodium silicate	Surface collector	
8.	Dispersant A	Control	Polyvinyl acetate	Dispersant B	
9.	#Control	Borate silicate	Citrus pectin	Dispersant A	

* The lowest number indicates the healthiest plot and the highest number indicates the unhealthiest plot (i.e., 1 = healthiest plot; 9 = unhealthiest plot).

** No observable difference among bracketed agents.

# Dead plants observed in test plots.

"Comparative Toxicities of Oils, Oil Fractions and Emulsifiers," Ecological Effects of Oil Pollution, ed.E.B. Cowell, London Institute of Petroleum, 1971.) Although not observed during testing, it is suggested that #2 fuel oil may have penetrated the soil and killed the plants' roots and rhizomes as well as stems and leaves. Subsequently, rhizomes from the surrounding soil invaded the plot, giving rise to the scant vegetation later observed there. The more viscous #6 fuel oil probably did not penetrate the soil. Consequently, underground portions of plants exposed to this oil were not affected.

The semiquantitative indexes described previously provided a means to suggest and rank the relative toxic response of each surface treatment agent for each test oil and control condition. The results are presented in Table B-16. A few trends are apparent. Note the relative position of the control plots. In the first observation period (February 10), the data suggest that most agents were associated with better-than-control plant response for the #2 and #6 fuel oils, and most produced diminished results with Arabian crude oil. Over the longer term, the data suggest that most agents are associated with a better-than-control or an equivalent-to-control recovery. It should be noted, however, that marsh reaction to various kinds of disturbances (including oil pollution) is commonly manifested by heavy growth and speciation changes.

The increased difficulty over time in distinguishing between different agent effects is apparent. Sodium silicate appears to be the least toxic agent. Although it seems that the surfactants may be toxic, it is difficult to extract more detailed conclusions from the limited data.

Many of the test plots became overgrown with pickleweed (Salicornia virginica) during the course of investigations. It is possible that this resulted from some subtle effect of oil contamination. However, examination of the surrounding area revealed that pickleweed was probably about to colonize the test area independently from human activity.

Quantitative Data--

Regression coefficients of height vs.time (i.e.,growth rates) were calculated for all data points on each plot and for the three smallest stems within each plot at each sampling period. (Calculations were based on methods developed by Robert R.Sokal and F. James Rohlf, Biometry, San Francisco: W.H. Freeman and Company.) Although the latter analysis was strongly biased toward young stems, the same bias applies to all plots. Furthermore, it is reasonable to assume that if long-term stunting occurred, it would be detected as a shorted minimal stem length in adversely affected plots. Short-term stunting that affected only stems that were growing when test agents and oils were applied might remain undetected.

Results of these regression analyses are displayed in Tables B-17 and B-18, along with the number of times that plants on each plot were measured, and the statistical significance of the difference of growth coefficients from zero. Statistical significance depends on the number of samples, the variation in growth rate among grass stems, and the growth rate of individual plants. Differences in the number of times each plot was sampled are attributable to tidal inundation of the test area during the first height-measurement sampling and to bank erosion that undercut some plots, TABLE B-17. REGRESSION COEFFICIENT - GROWTH RATE (cm/day) USING ALL DATA

Agent	Dry Control		Significance	Times Sampled	Wet Control		Significance	Times Sampled	#2 Fuel Oil		Significance	Times Sampled	Arabian Crude		Significance	Times Sampled	#6 Fuel Oil		Significance	Times Sampled
3% Sodium silicate	(1)	.0398	ns	3*	(6)	-.0180	ns	3	(13)	.0730	**	3	(17)	.0643	ns	3	(24)	.0997	ns	3
1% Xanthan gum	(2)	.0288	ns	3	(7)	.0411	**	3	(14)	.0971	ns	3	(19) (33)	.0863 .0522	ns ns	3 3	(23)	.1022	ns	3
1% Citrus pectin	(3)	.0129	ns	3	(8)	.0438	ns	3	(11)	.0357	ns	3	(18)	.0748	ns	3	(26)	-.0058	ns	3
3% Borate-silicate mixture	(4)	.0564	**	3	(9)	.0056	ns	3	(12)	.1137	ns	3	(20)	.0917	ns	3	(25)	.1096	ns	3
100% Poly-vinyl acetate	(5)	.0573	ns	3	(10)	.0345	ns	3	(15)	.0282	ns	3	(21) (29) (34)	.0980 .0496 .0898	ns ns ns	3 3 3	(27)	.0478	ns	4
Surface collector	(39)	.0573	ns	3					(42)	.0463	ns	2	(36)	.0284	***	3	(45)	.0815	ns	3
Dispersant B	(40)	.0366	ns	3					(43)	.0870	ns	2	(32) (37)	.0841 .0777	ns ns	3 3	(46)	.1141	**	3
Dispersant A	(41)	.0546	ns	3					(44)	.0968	**	3	(31) (38)	.0082 .1103	ns ***	3 4	(47)	.0650	ns	3
Control									(16)	.1242	ns	3	(22) (30) (35)	.0825 .0309 .0729	ns ns ns	3 3 3	(28)	.0479	ns	3

* 10 stems measured at each sample.
** Probability less than .05 that true growth rate is equal to 0.
*** Probability less than .01 that true growth rate is equal to 0.

ns = Growth rate is not significantly different from 0.

TABLE B-18. REGRESSION COEFFICIENT - GROWTH RATE (cm/day) USING THREE SHORTEST STEMS IN EACH PLOT

	Dry Control	Significance	Times Sampled	Wet Control	Significance	Times Sampled	#2 Fuel Oil	Significance	Times Sampled	Arabian Crude	Significance	Times Sampled	#6 Fuel Oil	Significance	Times Sampled
3% Sodium silicate	(1) .0516	ns	3*	(6) .0252	ns	3	(13) .0788	ns	3	(17) .0837	ns	3	(24) .0753	***	4
1% Xanthan gum	(2) .0301	ns	3	(7) .0488	ns	3	(14) .0938	ns	3	(19) .0448 (33) .0269	ns ns	4 3	(23) .0930	ns	4
1% Citrus pectin	(3) .0195	ns	3	(8) .0431	ns	3	(11) .0565	ns	3	(18) .0746	ns	4	(26) -.0072	ns	3
3% Borate-silicate mixture	(4) .0480	ns	3	(9) .0547	ns	3	(12) .0817	ns	3	(20) .0515	ns	4	(25) .0916	ns	4
100% Poly-vinyl acetate	(5) .0381	ns	3	(10) .0364	ns	3	(15) .0159	ns	3	(21) .0965 (24) .0192 (34) .0754	** ns ns	4 3 3	(27) .0614	**	4
Surface collector	(39) .0795	**	4				(42) .0741	ns	2	(36) .0048	ns	4	(45) .0899	***	4
Dispersant B	(40) .0126	ns	3				(43) .0210	ns	2	(32) .0643 (37) .0505	ns ns	3 4	(46) .0637	ns	4
Dispersant A	(41) .0642	****	3				(44) .0632	**	3	(31) .0357 (38) .0592	ns **	3 4	(47) .0642	**	4
Control							(16) .1748	ns	3	(22) .0615 (30) .0242 (35) .0518	ns ns ns	4 4 3	(28) .0246	ns	4

* 10 stems measured at each sample.
** Probability less than .05 that true growth rate is equal to 0.
*** Probability less than .01 that true growth rate is equal to 0.
**** Probability less than .001 that true growth rate is equal to 0.

ns = Growth rate is not significantly different from 0.

causing them to fall to the tidal flats below the marsh. These plots were no longer growing under equivalent conditions and could therefore not be considered valid samples.

For most agents and agent/oil combinations, no statistically significant growth rate coefficients are apparent in the data. However, it is important to exercise caution in interpreting these data, and the variations suggested should not be regarded as conclusive. Observed (nonsignificant) differences may result from factors other than treatment differences. Figure B-5 shows the location of all plots that displayed a significant growth rate coefficient in the regression analyses. Some scatter is apparent, but there also seems to be some clustering toward the shoreline.

In plots that were severely affected by agents and/or oil, many dead plants (height recorded as 0. cm) were initially present. The later samples included stems that were equivalent in height to many in less severely affected plots. It is not known whether these stems grew from rhizomes initially present in the soil and stimulated by the testing or from rhizomes that invaded from adjacent areas of the marsh. Whatever their origin, the sudden presence of tall stems is reflected in a high calculated growth rate that may not reflect the true situation.

Further testing using modified techniques will be necessary to conclusively identify and quantify toxic responses.

PRELIMINARY FIELD TESTS - BEACHES

Preliminary field tests of surface treatment agent effectiveness and application techniques were conducted in the test tank previously described. Most of the beach tests were performed concurrently with tests of agents on salt marsh. Movable 0.3-square-meter trays that held simulated beaches made of sand and of cobble/gravel/sand mixtures were used in the tank.

The purposes of the preliminary field tests were:

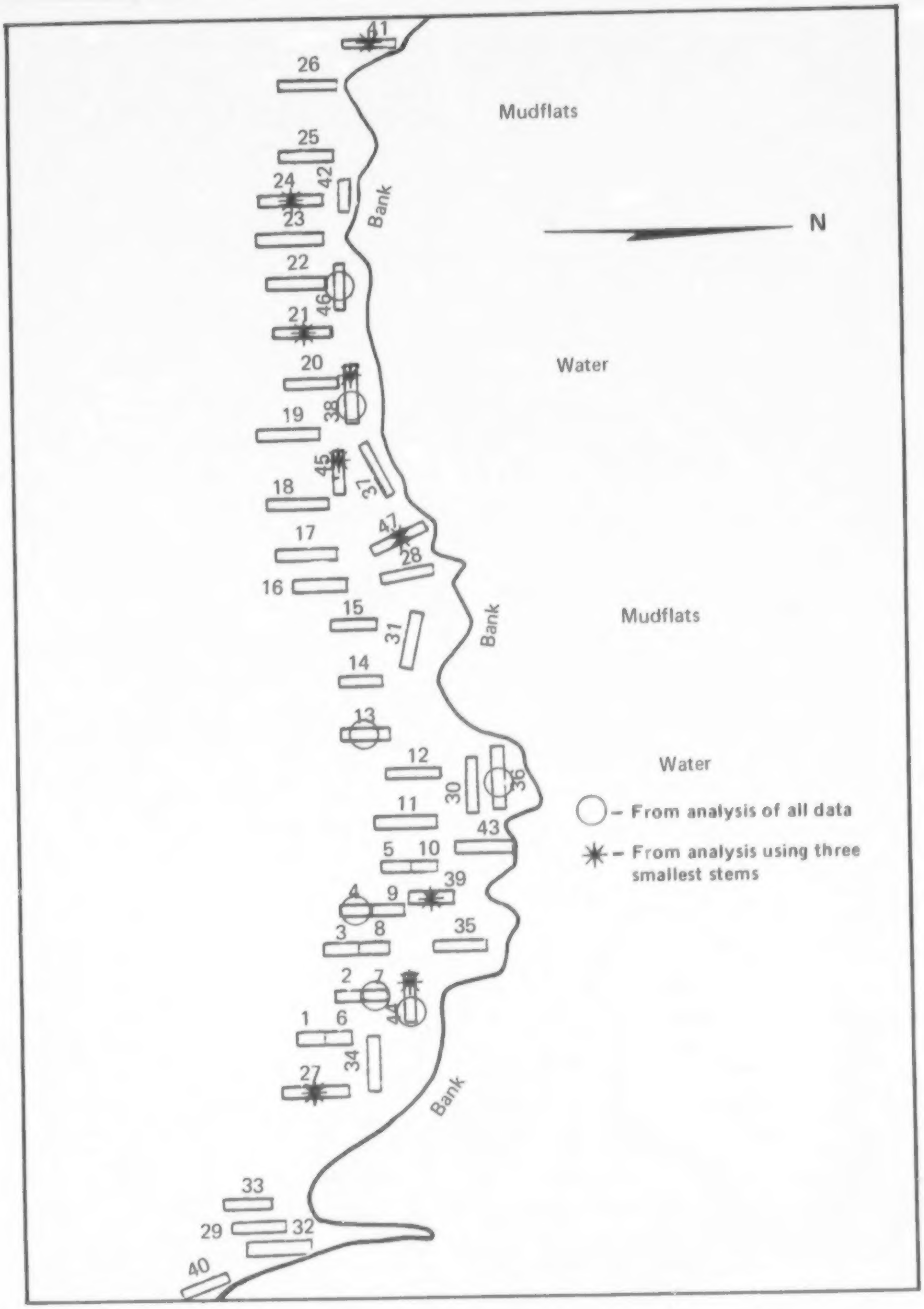
* To gain operational experience in the use of surface treatment agents

* To evaluate the durability of agents on various beach substrates

* To evaluate different agent application equipment and methods of removing the agent

* To determine which agents should be recommended for full-scale field tests

Three series of preliminary field tests were conducted. The purpose of the first series was to evaluate the durability of the film-forming agents and the ease of flushing of oil from these agents on sand and on cobble/gravel/sand test beaches, under both wet and dry substrate conditions. The film-forming agents tested were sodium silicate, borate-silicate mixture, citrus pectin, xanthan gum, and polyvinyl acetate. Tide and wave actions were simulated in the tank for these tests. In the second series, additional tests



Mudflats
Water
Mudflats
Water
Bank
Bank
Bank
N
○ – From analysis of all data
✳ – From analysis using three smallest stems
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42
24
23
22
46
21
20
38
19
45
37
18
47
17
28
16
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43
5
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39
4
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3
8
35
2
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44
1
6
34
27
33
29
32
40

Figure B-5. Location of plots with growth rates significantly different from zero.

were conducted with the two film-forming agents that proved successful in the first series, polyvinyl acetate and xanthan gum. In the tests different application techniques, agent concentrations, and agent drying times were evaluated and the two agents' resistance to oil contamination and oil penetration was assessed. The third test series evaluated four surfactants, using two application techniques to determine the effectiveness of the surfactants in preventing or reducing oil contamination on test beaches. Surfactants tested were the surface collector, dispersant A, dispersant B, and dispersant C.

Test Procedures

Test Beach Construction--

Test beaches were constructed on 0.3-square-meter trays that slide into individual cells in the test tank. The sand beaches were composed of about 23 kg of commercially available sand about 75 mm deep. The cobble/gravel/sand beaches consisted of a 25-mm layer of sand overlaid with a layer of rounded gravel (less than 25-mm diameter) and with 10 to 15 cobbles (75-mm to 150-mm maximum diameter).

Test Series 1

- Test beaches were constructed for each test.
- The lower half of each beach was sprayed with salt water.
- Borate-silicate mixture, sodium silicate, citrus pectin, and xanthan gum were premixed (using an electric blender) into water suspensions at the concentrations recommended by TRI. The agents were then applied to each test beach by spraying at 1.75 kg per sq cm (25 psi) with a garden sprayer (7.6-liter capacity). The polyvinyl acetate was used undiluted and applied with a paint-sprayer/air-compressor system at 4.2 kg per sq cm (60 psi).
- The agents were allowed to dry for varying periods of time and then each beach was submerged under water in the test tank for 10 minutes to simulate tidal action.
- The test beaches were retracted to a higher position in the tank and subjected to simulated wave action for 5 minutes.
- The agent on each test beach was examined to determine the film durability and integrity.
- No oil was used in test series 1.

Test Series 2

- Test beaches were constructed and prepared for each test as in test series 1.
- Xanthan gum, when applied dry, was sprinkled by hand on the test beaches.

- * A hydraulic spraying system was used for polyvinyl acetate and xanthan gum solutions.

- * After application, each agent was allowed to dry for a given period of time, and the test beaches were then partially submerged in the tank. Five hundred mls of Arabian crude oil was added to each test cell, and simulated wave action was sustained for 5 minutes.

- * After the wave action ceased, the test beaches were retracted from the water and flushed with a water spray at 1.75 kg per sq cm (25 psi) to test the ease of flushing the agent-coated beach.

- * A segment of test beach was cut and removed from a representative area and examined under shortwave ultraviolet light to test for oil penetration. The aromatic content of crude oil exhibits a characteristic fluorescence which, when detected on the side of the sample segment, indicates the degree of oil penetration.

Test Series 3, Surfactants

- * Test beaches were constructed and prepared for each test as in test series 1.

- * Two agent application techniques were tried with the surfactants.

  - All four agents were sprayed onto partially submerged test beaches and into the water in front of the beaches. Five hundred mls of crude oil was then introduced into each test cell, and wave action was sustained for 5 minutes.

  - The test beaches were partially submerged in the tank, and 500 or 750 ml of crude oil was placed into each test cell.

  - Wave action was initiated and the agent sprayed onto the foreshore of the beach and into the water in the surf zone in front of the advancing oil slick.

- * Oil penetration into the simulated beaches was determined as described in test series 2.

Results

Detailed results of the test series on beaches are given in Tables B-19, B-20, and B-21 and discussed below.

Ineffective Agents. Three film-forming agents proved completely ineffective as surface treatment agents on sand or gravel/cobble/ sand beaches. These were sodium silicate, borate-silicate mixture, and citrus pectin. All three agents either dissolved or were mechanically fragmented by wave action and/or by submergence in water. Further tests of the three agents were discontinued.

TABLE B-19. SURFACE TREATMENT AGENT BEACH TEST, SERIES 1

Test Number	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	1.10
Agent Tested	Sodium silicate	Sodium silicate	Citrus pectin	Citrus pectin	Borate-silicate mixture	Borate-silicate mixture	Xanthan gum	Xanthan gum	Polyvinyl acetate (Amsco 3011)	Polyvinyl acetate Amsco 3011)
Beach Type	Sand	Cobble/ gravel/sand	Cobble/ gravel/sand	Cobble/ gravel/sand	Sand	Cobble/ gravel/sand	Sand	Cobble/ gravel/sand	Sand	Cobble/ gravel/sand
Water temperature (C)	10	7	10	7	10	7	10	7	10	7
Wind speed (m/sec)	0.0	2.2	0.0	2.2	0.9	2.2	0.0	2.2	0.0	2.2
Application Method and Spray Pressure	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Hudson sprayer, 1.75 kg/ sq cm (25 psi)	Air compressor spray-paint gun, 4.2 kg/sq cm (60 psi)	Air compressor spray-paint gun, 4.2 kg/sq cm (60 psi)
Volume of Agent Used (ml)	500	500	1000	450	455	500	1000	500	300	200
Percent Dilution	3	3	1	1	3	3	1	1	100	100
Application Rate	50 g/sq m	50 g/sq m	33 g/sq m	45 g/sq m	45 g/sq m	100 g/sq m	33 g/sq m	17 g/sq m	1000 ml/sq m	667 ml/sq m
Time Required to Spray Agent (sec)	60	45	40	45	40	50	50	50	110	90
Agent Drying Time (hr:min)	2:15	2:45	1:55	2:10	1:40	2:25	2:05	2:45	1:40	1:40
Results of Agent Test	Agent dissolved into water column; none remained on beach	Agent dissolved into water column; none remained on beach	Agent dissolved into water column; none remained on beach	Agent dissolved into water column; none remained on beach	Agent dissolved into water column; none remained on beach	Agent dissolved into water column; none remained on beach	Most of the agent remained on dry beach section; some was removed from wet beach	Some agent left on cobbles on dry section less on wet section; overall, less remained than on sand	Agent did not dry; most dissolved; some remained, but very soft	Agent did not completely dry on sand; agent did dry on cobbles and remained on cobbles after test
Comments	Water surface covered with foam during test	Some foam on water surface during test	--	Dye used to identify agent; some dye remained, agent dissolved	Foam and scum appeared on surface during test	--	Some froth and scum appeared on beach	--	Difficult application, sprayer clogged repeatedly	Difficult application, sprayer clogged repeatedly

NOTES: Water salinity - 32 ppt
Air temperature - 11°C
Cloud cover - 95% during Test 1.6, 100% during all other tests
Surface condition - 50% wet, 50% dry

TABLE B-20. SURFACE TREATMENT AGENT BEACH TEST, SERIES 2

Test Number	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	2.10
Agent Tested	Xanthan gum (dry powder)	Xanthan gum (dry powder)	Xanthan gum	Xanthan gum (dry powder)	Xanthan gum (dry powder)	Xanthan gum	Polyvinyl acetate (Amsco 3011)	Polyvinyl acetate (Amsco 3011)	Control beach	Control beach
Beach type	Sand	Cobble/ gravel/sand	Sand	Sand	Cobble/ gravel/sand	Sand	Sand	Sand	Sand	Sand
Water temperature (°C)	9	9	9	9	9	7	9	7	6.5	7
Air temperature (°C)	10	10	10	10	10	19	10	19	18	16
Wind speed (m/sec)	1.0	1.0	3.5	3.5	3.5	1.0	1.0	1.0	1.0	1.0
Percent Cloud Cover	None	None	None	None	None	50% hazy	None	50% hazy	None	50% hazy
Application Method and Spray Pressure	Sprinkled powder on beach; applied water spray	Sprinkled powder on beach; applied water spray	Hudson sprayer, 1.75 kg/cm (25 psi)	Sprinkled powder on beach; applied water spray	Sprinkled powder on beach; applied water spray	Sprayed agent on beach with hydraulic sprayer, 14 kg/sq cm (200 psi)	Hudson sprayer, 1.75 kg/sq cm (25 psi)	Sprayed agent on beach with hydraulic sprayer, 14 kg/sq cm (200 psi)	N.A.	N.A.
Volume of Agent	50 g	50 g	1000 ml	100 g	100 g	1000 ml	400 ml	500 ml	N.A.	N.A.
Percent Dilution	N.A.	N.A.	N.A.	N.A.	N.A.	1	100	100	N.A.	N.A.
Application Rate	166 g/sq m	166 g/sq m	33 g/sq m	333 g/sq m	333 g/sq m	33 g/sq m	1333 ml/sq m	1666 ml/sq m	N.A.	N.A.
Time Required to Spray Agent (sec)	120 (dust and spray)	120 (dust and spray)	90	120 (dust and spray)	120 (dust and spray)	5	240	15	N.A.	N.A.
Agent Drying Time (hr:min)	0:10	0:10	2:40	2:30	2:30	0:30	2:30	0:30	N.A.	N.A.

(Continued)

TABLE B-20 (Continued)

Test Number	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	2.10
Agent Tested	Xanthan gum (dry powder)	Xanthan gum (dry powder)	Xanthan gum	Xanthan gum (dry powder)	Xanthan gum (dry powder)	Xanthan gum	Polyvinyl acetate (Amsco 3011)	Polyvinyl acetate (Amsco 3011)	Control beach	Control beach
Volume and Type of Oil Applied (ml)	None	None	500, crude	None	500, crude	500, crude	500, crude	500, crude	500, crude	500, crude
Percent Oil Coverage on Beach After Test	N.A.	N.A.	60	N.A.	60	40-50	10	20-30	80	20-30
Depth of Oil Penetration (cm)	N.A.	N.A.	<0.6	N.A.	N.A.	<0.2	0.6	0.6	1.3 to 0.6	1.3
Results of Agent Test	No difference in jelling on wet and dry surfaces; most of agent film broke up in wave action and was washed off beach	No difference in jelling on wet and dry surfaces; some agent washed off, particularly from sand and gravel; agent remained on cobbles	Jelled agent remained on more than 50% of beach; oil easily washed off jelled agent with water spray	Agent flaked off under wave action; almost none remained on test surface	Agent remained on cobbles and pebbles; oil on agent easily washed off with water spray	Agent remained on beach above and below wave splash zone; oil was flushed off agent easily	Agent dried to hard surface on dry beach, softer on wet beach; agent remained on beach - oil flushed off easily with water spray	Agent had not dried sufficiently and dissolved in water column; some remained, and oil on remaining agent washed away easily	Oil remained on approximately 80% of beach, penetration of 25 cm in some areas	Agent remained on beach above and below wave splash zone; oil was flushed off agent easily
Comments	--	--	Agent still soft and flexible at test time	Agent jelled to firm jell on dry sand; still runny on wet sand	--	Area of beach in wave zone was eroded away and agent on that area was also washed away	Difficult to apply with Hudson sprayer, frequent clogging	Area of beach in wave zone eroded away	--	Oil was flushed off part of beach but tended to percolate into sand

NOTES: Water salinity - 32 ppt
Surface condition - 100% dry for Test 2.6, 50% wet and 50% dry for all other tests
N.A. - not applicable

TABLE B-21. SURFACE TREATMENT AGENT BEACH TEST, SERIES 3

Test Number	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10
Agent Tested	Dispersant C	Dispersant B	Dispersant A	Surface collector	Dispersant B	Dispersant A	Dispersant A	Dispersant A	Dispersant C	Control beach
Beach Type	Sand	Sand	Sand	Sand	Sand	Cobble/ gravel/sand	Cobble/ gravel/sand	Sand	Sand	Sand with several cobbles
Water Temperature (°C)	6.5	6.5	6.5	10	10	10	8	8	8	8
Air Temperature (°C)	18	18	18	18	18	18	12	12	12	12
Wind Speed (m/sec)	0.8	0.8	0.8	2.2	2.2	2.2	0.5	0.5	0.5	0.5
Percent Cloud Cover	Clear	Clear	Clear	80	80	80	20	20	20	20
Application Method and Spray Pressure	Sprayed agent on beach with air compressor spray gun at 4.2 kg/ sq cm (60 psi)	Sprayed agent on beach with air compressor spray gun at 4.2 kg/ sq cm (60 psi)	Sprayed agent on beach with air compressor spray gun at 4.2 kg/ sq cm (60 psi)	Sprayed agent on beach and on water with Hudson sprayer at 1.75 kg/ sq cm (25 psi)	Sprayed agent on beach and into water ahead of advancing oil slick with Hudson sprayer at 1.75 kg/sq cm (25 psi)	Air compressor and spray gun onto cobbles at 4.2 kg/sq cm (60 psi) and and into water ahead of oil slick	Sprayed agent into water ahead of advancing oil slick with Hudson sprayer at 1.75 kg/ sq cm (25 psi)	Sprayed agent into water ahead of advancing oil slick with Hudson sprayer at 1.75 kg/ sq cm (25 psi)	Sprayed agent into water ahead of advancing oil slick with Hudson sprayer at 1.75 kg/ sq cm (25 psi)	N.A.
Volume of Agent	560 g	100 g	500 g	40 ml	75 ml	200 ml	500 ml	500 ml	500 ml	N.A.
Percent Dilution	10	100	2	100	100	2	2	2	10	N.A.
Application Rate	186 ml/sq m	333 ml/sq m	33 ml/sq m	133 ml/sq m	250 ml/sq m	13 ml/sq m	33 ml/sq m	33 ml/sq m	166 ml/sq m	N.A.
Time Required to Spray Agent (sec)	90	30	240	10	30	30	60	60	50	N.A.

(continued)

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TABLE B-21 (Continued)

Test Number	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	3.10
Agent Tested	Dispersant C	Dispersant B	Dispersant A	Surface collector	Dispersant B	Dispersant A	Dispersant A	Dispersant A	Dispersant C	Control beach
Percent Oil Coverage on Beach After Test	30	30	80	< 5	5-10	30	60	< 10	80-100	80-100
Depth of Oil Penetration (cm)	1.3	1.3	1.3-1.9	Occasional spots 0.6 cm below surface	Occasional spots 0.3-0.6 cm below surface	Some penetration	N.A.	No penetration	Penetration greater than control - 3.8	1.3
Results of Agent Test	Some oil dispersion on water surface; however, oil penetrated beach	Oil dispersed to some extent on water surface; however, oil penetrated beach	No oil dispersion on water surface seen; oil penetration similar to control beach	Very effective; only some oil on upper splash zone; tended to drive oil off in small slicks	Excellent effectiveness; oil dispersed into water column; little remained on beach	Fair effectiveness; cobbles remained oil-free; some oil on sand and gravel	Sand and pebbles in lower half of beach were coated with a light covering of oil; pebbles had more oil than rocks	Excellent effectiveness on sand; oil was dispersed into water column; very little on beach	Not effective; oil surface contamination	Cobbles on beach coated with oil
Comments	Spraying surfactant dispersants onto beach prior to arrival of oil is not effective in reducing oil contamination	--	--	--	--	--	--	--	--	--

NOTES: Water salinity - 32 ppt
Surface condition - 100% wet for Test 3.4, 50% wet and 50% dry for all other tests
Agent drying time - in Test 3.9, BP 100-WD was allowed to dry for 10 minutes
Volume and type of oil applied - 500 ml Arabian crude oil
N.A. - not applicable

Xanthan Gum and Polyvinyl Acetate. Xanthan gum proved fairly effective. It provided a soft, jellylike barrier film on both sand and gravel/cobble/sand test beaches and was most effective when applied to dry test beaches in a premixed 1% solution. It retained film integrity somewhat less effectively when applied to wet surfaces. When xanthan gum was applied as a dry powder and then sprayed with water, it formed a more rigid film; but the film tended to break easily under wave action on a sand test beach. On cobble/gravel/sand test beaches the film formed from dry powder was more successful and did maintain film integrity. In all cases where film integrity was maintained, a water spray easily flushed oil from the surface coated by xanthan gum.

When allowed sufficient time to dry, polyvinyl acetate also provided an effective protective film on both sand and cobble/ gravel/sand test beaches. The drying time is critical in the use of polyvinyl acetate. On tests where polyvinyl acetate was still wet, it dissolved into the water column and lost film integrity. Polyvinyl acetate tended to dry faster on cobble and gravel than on sand. Where the polyvinyl acetate film integrity was maintained, oil penetration into the beaches was limited, and oil was easily flushed from the agent-coated beach surface by a water spray.

The films of both xanthan gum and polyvinyl acetate can be removed from a sand test beach with a high-pressure water spray, which breaks the film into small particles. However, it is considerably more difficult to remove xanthan gum and polyvinyl acetate films from cobble and gravel surfaces.

Several cobbles coated with xanthan gum and with polyvinyl acetate were left to dry for 24 hours. The xanthan gum dried to a firm, nonbrittle crust, and polyvinyl acetate dried to a hard, paintlike coating. The agent-coated cobbles were subjected to steam cleaning by a portable steam cleaner for 5 minutes with no apparent effect on either agent.

Surface Collecting Agent. The surface collector proved very effective in reducing oil contamination of the test beach, although this result was quite different from those of the tests performed on the collecting agent in the laboratory. TRI tested it in the concentration recommended by the manufacturer, which is 1 gallon per 2 linear miles of oil slick perimeter, or approximately 1.2 ml per linear meter of beach. At this concentration the surface collector proved ineffective. In the tank tests, however, higher concentrations were used. The agent was sprayed onto the test beach and into the water in front of the beach, where it successfully repelled oil from most of the beach surface.

Dispersing Agents. When they were applied properly, the dispersing agents, A, B, and C, effectively protected the test beaches from oil contamination. When they were used like the film-forming agents and the collecting agent (i.e., when they were sprayed onto the shoreline before tidal and wave actions were begun), the dispersing agents were ineffective and in one case caused more oil penetration than occurred on the control test beach. When they were sprayed into the water (i.e., surf zone) ahead of the advancing oil slick, the dispersing agents effectively prevented contamination of the sandy test beaches. These agents were somewhat less effective on cobble/gravel/sand test beaches; some oil contaminated the cobble/gravel/sand substrate, but there was considerably less contamination than on the control beach.

Application Equipment. Three types of equipment for applying liquid agents were evaluated during the preliminary tests. They were:

- Hand-operated garden-type sprayer

- Air compressor (pneumatic) paint spray gun

- Hydraulic sprayer

The hydraulic sprayer was the most effective system for applying the two film-forming agents, xanthan gum, and polyvinyl acetate. Due to their viscosity, both agents require high-pressure application to provide an even coating in a reasonable amount of time. When the lower pressure garden sprayer (1.75 kg per sq cm, or 25 psi) and the pneumatic paint sprayer (4.2 kg per sq cm, or 60 psi) were used to apply these agents, the spray nozzle clogged frequently, which increased spraying time and made it difficult to apply the agent evenly. However, the lower pressure spraying systems were effective in applying the surfactants.

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APPENDIX C

BIOASSAY OF EASTERN BLUE CRAB WITH SELECTED SURFACE TREATMENT AGENTS

INTRODUCTION

Two surface treatment agents - polyvinyl acetate (PVA) and xanthan gum - were selected for the static bioassay testing (96-hour TLM). First-stage juveniles of the commercially important blue crab, *Callinectus sapidus*, were used as test organisms. The concentrations tested were in ranges believed to occur in seawater after an agent film had been removed from the beach and marsh shorelines.

MATERIALS AND METHODS

Juvenile* blue crabs were furnished by Sea Plantations, Inc., Salem, Massachusetts. Approximately 140 crabs were collected from the tidal flats of Delaware Bay on 16 October 1977 and 24 October 1977, packed in seawater and seaweed, and air-shipped to Salem. The crabs were held in aquarium tanks (pH = 7.6, salinity = 32 ppt, temperature = 21°C) and fed euphausiid shrimp and small pieces of fish. On 3 November 1977, the crabs were air-shipped in plastic bags containing wet seaweeds to Pacific Environmental Labs in San Francisco. There was no apparent stress or mortality of the crabs due to shipment.

The crabs were acclimated to test conditions in a 30-gallon plexiglass aquarium tank for 90 hours. Compartments within the tank kept the larger crabs separated from the smaller ones. The tank contained filtered Pacific Ocean seawater (pH = 7.8 and salinity = 30 ppt) from Steinhart Aquarium at Golden Gate Park in San Francisco. Temperature of the seawater during acclimation was maintained at 18 ±1°C. The crabs were fed brine shrimp during the acclimation period but were not fed during the 96-hour test period.

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* Because of the severe 1976 winter in the east, post-larval (megalops) crabs, the prescribed test organism, were 1 to 2 months late. When they finally did appear in the water column, the megalops populations were extremely sparse and difficult to locate. After numerous plankton tows failed to produce any megalops, and efforts to hatch eggs from five sponge crabs similarly failed, Sea Plantations turned their efforts in October to obtaining small juvenile crabs.

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The bioassay test was performed in accordance with the method as outlined in "Standard Methods for the Examination of Water and Wastewater," 14th Edition, APHA-AWWA-WPCF, and "Guidelines for Performing Static Acute Bioassays in Municipal and Industrial Wastewaters," 1976, of the California Water Resources Control Board and Department of Fish and Game.

The tests were performed in seven 19-liter plexiglass aquaria. The volume of the control and each of the test concentrations were 10 liters. The control and dilution water used was filtered seawater from Steinhart Aquarium. The liquid depth of each tank was 12.5 ±0.2 cm. Compressed air was used for aeration.

The test concentrations used were selected (1) to reflect concentrations that would occur after the agents were flushed from the beach and marsh shorelines, (2) to bracket the lethal and nonlethal toxicity levels of the two agents, and (3) to make the best use of what turned out to be a small sample size. Estimates of agent concentration after flushing were obtained by taking the application quantities per unit area established during the field tests and estimating the runoff from this area into a small marsh channel. By assuming that this receiving water was a closed unit and of minimum volume, worst-case concentrations were estimated (10% for xanthan gum and 5% for PVA).* The maximum PVA concentration was estimated at half that for xanthan gum because PVA tends to adhere better to the plant surface and less was applied per unit area.

In an attempt to locate the sublethal toxicity limits for both agents, the remaining test concentrations were obtained by multiplying the maximum concentrations by a factor of 0.3. In this way, a geometric series of concentrations, with the lower limits below 1%, were obtained. Test concentrations by volume of PVA were 5, 1.5, and 0.45%; test concentrations by volume of xanthan gum were 10, 3, and 0.9%.

So that size differential would not become a confounding variable, 70 of the smallest blue crabs received from Sea Plantations were selected as the test organisms. These crabs were between 6 millimeters and 32 millimeters in length (average = 12 millimeters) and approximately 45 to 75 days old. With only 70 organisms, the tests were limited to three concentrations of each agent, 10 organisms per tank. One 10-crab tank served as the control for both agents. Crabs were placed in the tanks so that each tank contained comparable size distributions which, in turn, reflected the distribution of the test population.

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* Concentrations referred to in this report reflect the percent by volume of the test agents in seawater. The pre-dilution strengths of the agents were the same as they were tested in the field: 100% for the PVA and 1% for the xanthan gum.

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RESULTS AND DISCUSSION

Mortality data for the 96-hour TLM are listed in Table C-1 and displayed graphically in Figures C-1 and C-2. Both the PVA and xanthan gum agents were acutely toxic to all organisms in the highest concentration tanks. The PVA seemingly affected the crabs more quickly than did the xanthan gum. Though only two of the crabs in 10% xanthan gum were dead after 24 hours, six others were moving very slowly by that time. By 48 hours, all 10 crabs in the 10% xanthan gum had died.

No mortality occurred in the tanks subjected to the lowest concentrations of each agent. The intermediate PVA concentration (1.5%) was not as immediately toxic to the crabs as was the 5% concentration, but four crabs died between the 48- and 72-hour reading and another four died by the end of the test. The 10 crabs subjected to the intermediate xanthan gum concentration all survived. All 10 of the control crabs survived. None of the surviving crabs in the test showed any signs of paralysis or stress. Although the sizes of the crabs varied between 6 mm and 32 mm, there was no apparent correlation between the size and mortality of the test animals used.

During the test, two of the blue crabs molted (one each in 3% and 0.9% xanthan gum concentrations). Both of these molted blue crabs survived the 96-hour test period with no apparent paralysis or stress.

Water quality data taken during the tests (Table C-2) suggest that a low pH might have contributed to PVA's rapid and acute toxicity. Figure C-3 shows that as the concentration of PVA increased, initial pH and alkalinity (a measure of the solution's buffering capacity) decreased. In the 5% PVA tank, the pH decreased to 4.2 and remained at that level for at least 48 hours. While the pH decreased to 5.9 in the 1.5% tank, within 24 hours the pH had climbed back to more than 7 with no apparent effect on mortality.

Dissolved oxygen levels fluctuated considerably throughout the tests (Figures C-4 and C-5). At all three concentrations of xanthan gum, the oxygen

TABLE C-1. STATIC ACUTE BIOASSAY MORTALITY (%)

		Initial	24 Hours	48 Hours	72 Hours	96 Hours
Control		0	0	0	0	0
PVA	5.0%	0	80	100	100	100
	1.5%	0	0	0	40	80
	0.45%	0	0	0	0	0
Xanthan gum	10.0%	0	20	100	100	100
	3.0%	0	0	0	0	0
	0.9%	0	0	0	0	0

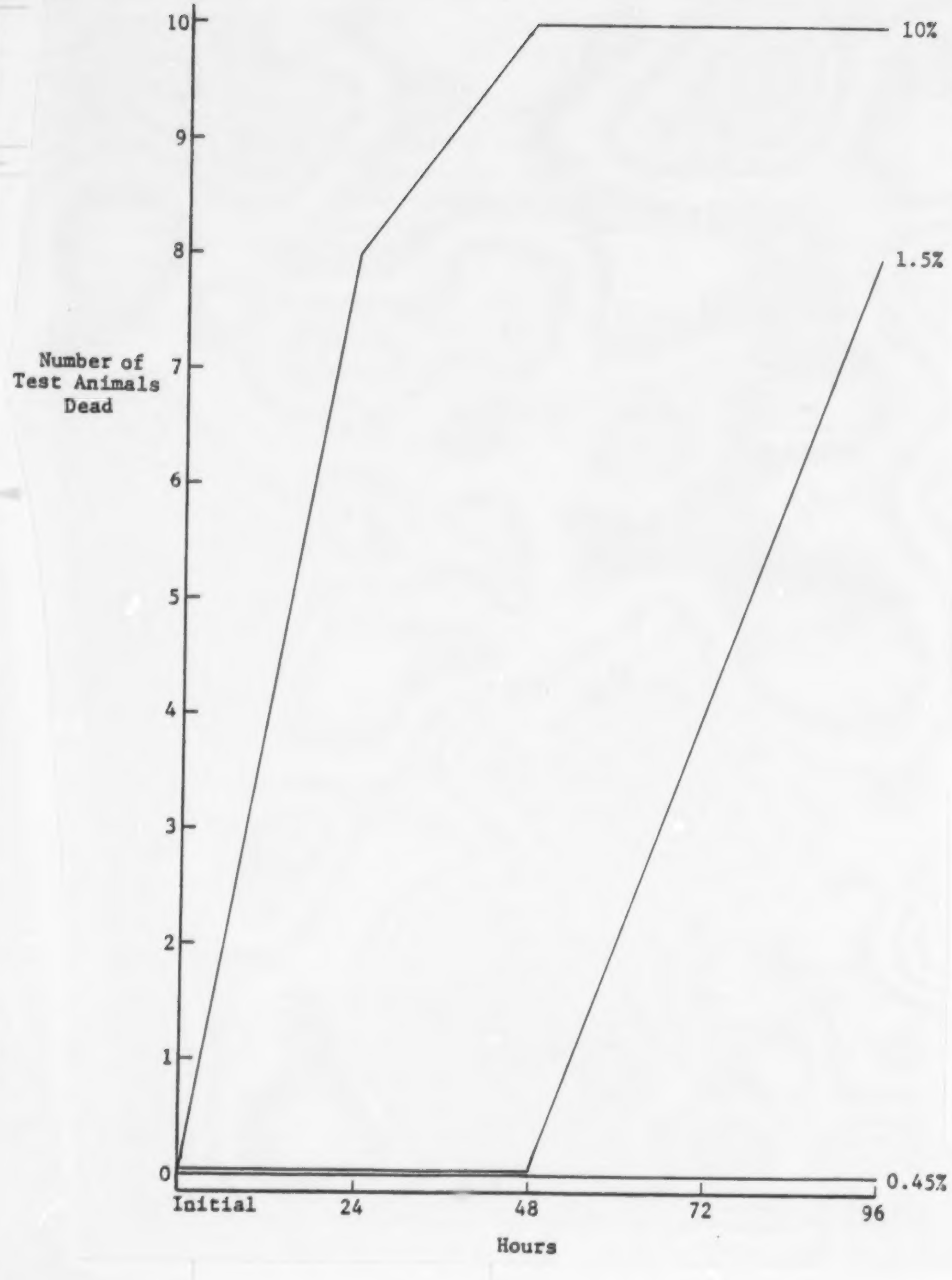

Figure C-1. Static acute bioassay mortality -- polyvinyl acetate.

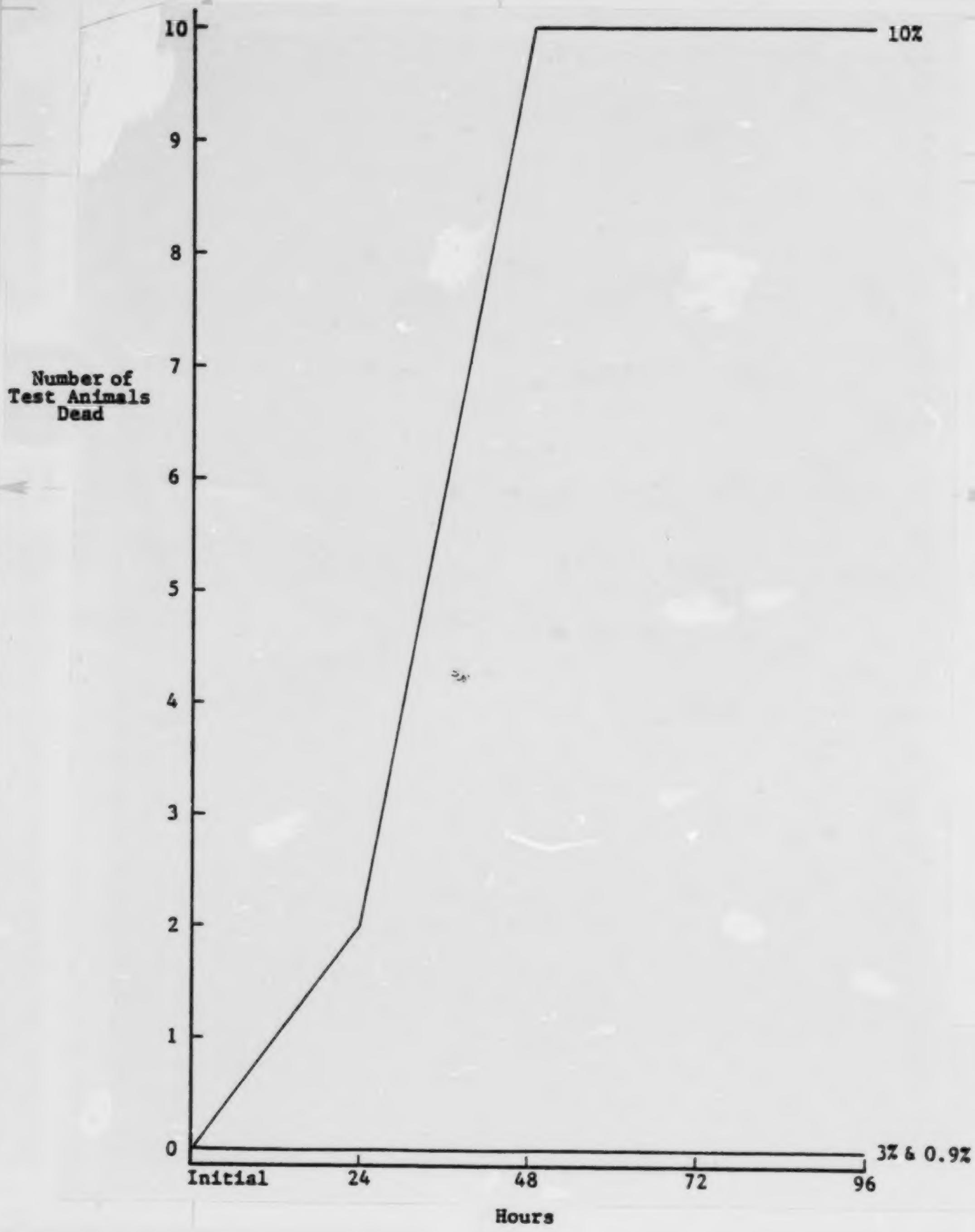

Figure C-2. Static acute bioassay mortality -- xanthan gum.

TABLE C-2. ALKALINITY, pH, AND DISSOLVED OXYGEN DURING THE 96-HOUR TLM

		Initial			24 Hours			48 Hours			72 Hours			96 Hours		
		Alk.	pH	D.O.	Alk.	pH	D.O.	Alk.	pH	D.O.	Alk.	pH	D.O.	Alk.	pH	D.O.
Control		144	8.0	8.6	--	7.9	8.1	--	7.8	8.0	--	7.8	8.0	--	7.7	7.7
PVA	5.0%	1.0	4.2	8.3	--	4.2	8.9	--	4.3	8.6	--	--	--	--	--	--
	1.5%	89	5.9	8.5	--	7.2	8.3	--	7.2	3.4	--	7.2	2.6	--	7.5	4.5
	0.45%	126	6.9	8.6	--	7.4	2.6	--	7.8	8.0	--	7.9	8.2	--	7.9	8.0
Xanthan gum	10.0%	146	8.0	8.4	--	7.1	3.0	--	7.7	7.8	--	--	--	--	--	--
	3.0%	146	8.1	8.5	--	7.6	6.2	--	7.7	7.6	--	7.8	7.6	--	7.7	7.0
	0.9%	146	8.1	8.6	--	7.8	7.4	--	7.9	8.4	--	7.9	8.2	--	7.9	7.8

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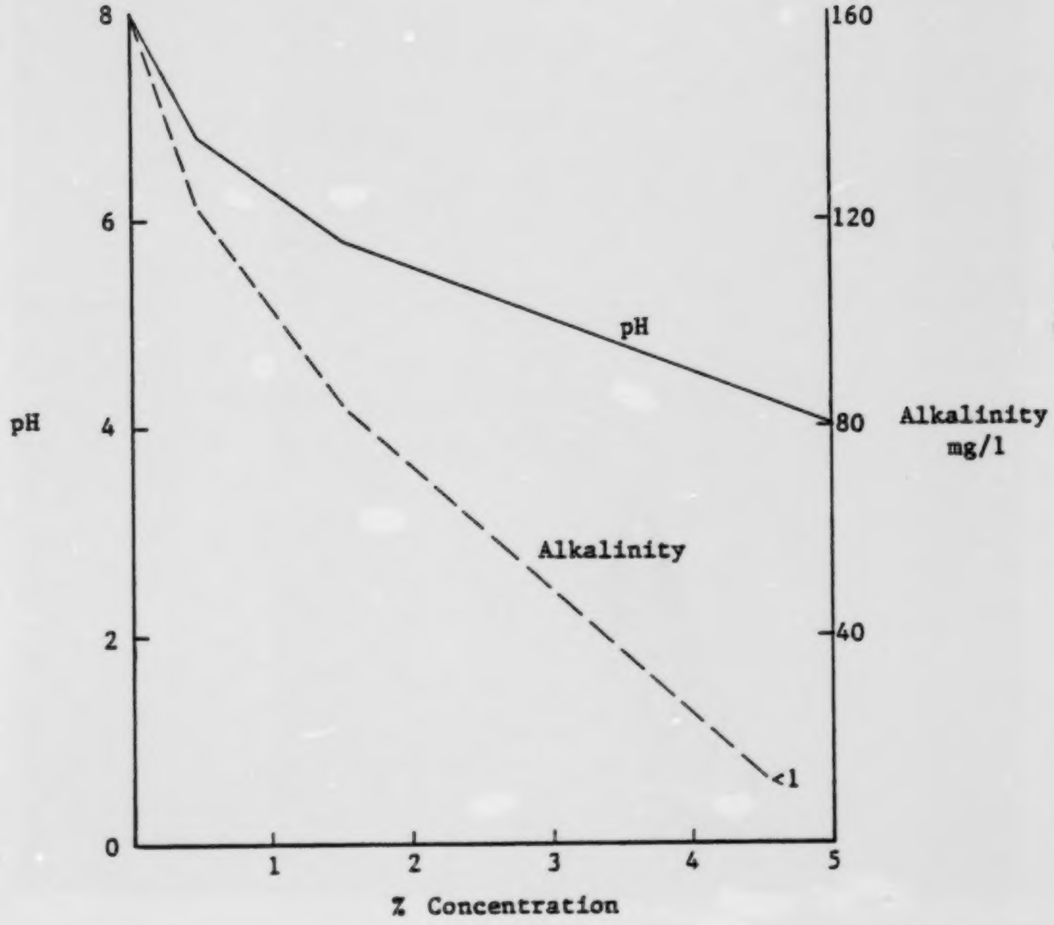

Figure C-3. Effect of different concentrations of PVA on alkalinity and pH in the test tanks.

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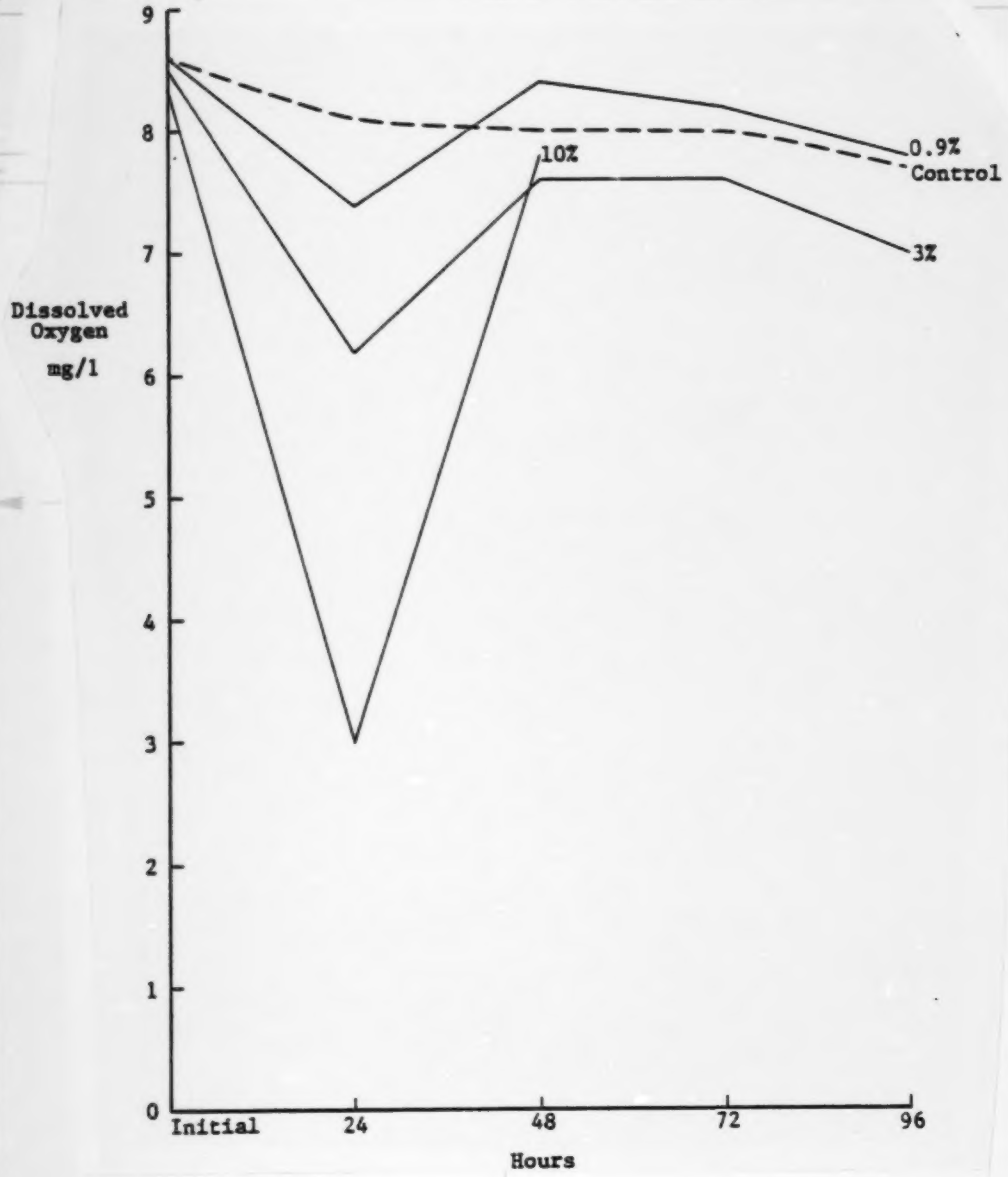

Figure C-4. Dissolved oxygen fluctuations -- xanthan gum.

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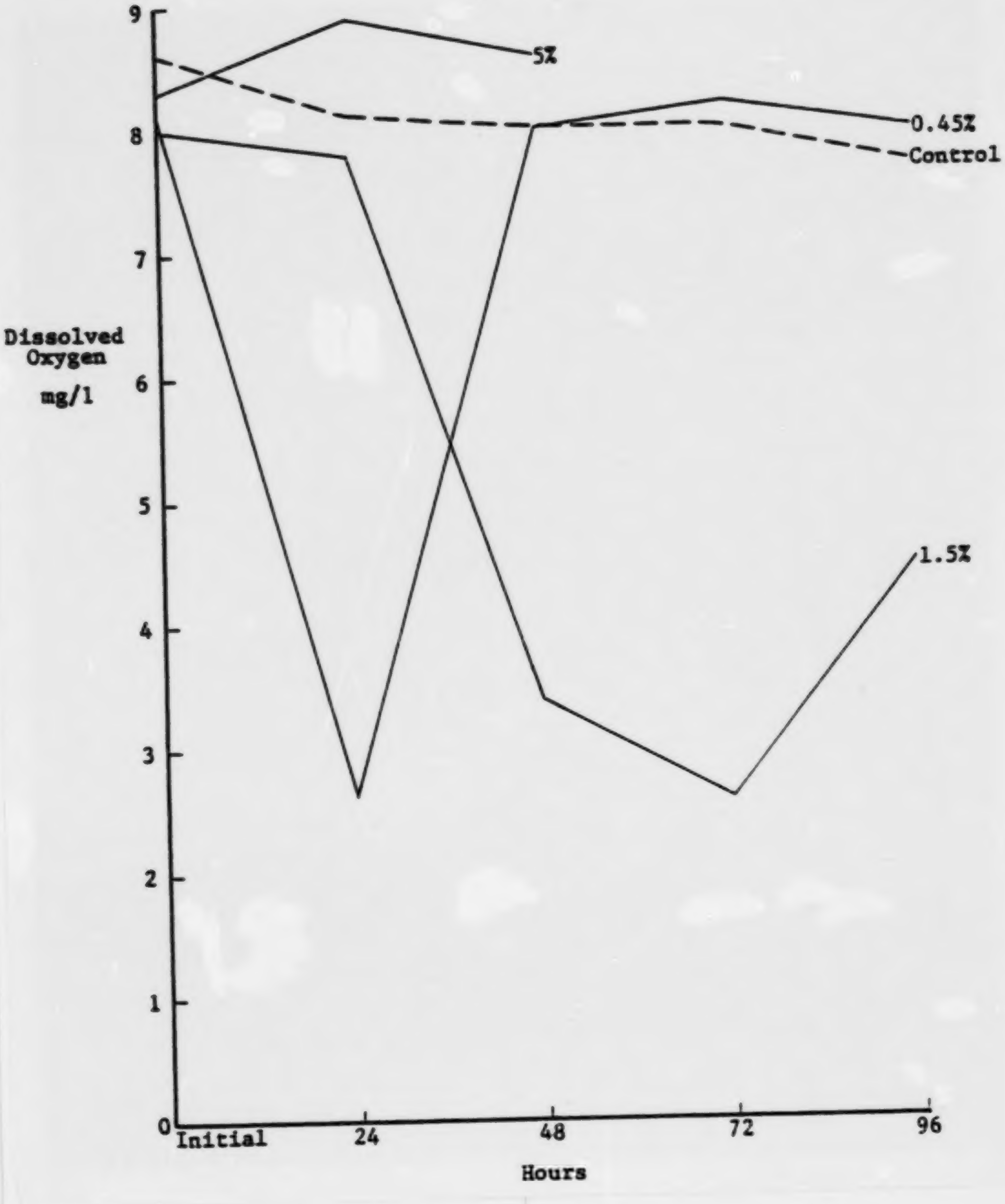

Figure C-5. Dissolved oxygen fluctuations -- polyvinyl acetate.

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level decreased during the first 24 hours of the test before returning to control levels. The dissolved oxygen in the 10% tank dropped to 3.0 milligrams per liter, possibly contributing to the narcosis observed in six of the surviving eight crabs in that tank. Oxygen sags, however, were not necessarily associated with mortality. The oxygen level in the 0.45% PVA tank dropped to 2.6 milligrams per liter during the first 24 hours with no adverse effects. Thus, while it is possible that the loss of dissolved oxygen contributes to the mortality of the crabs, especially when the crabs are under stress due to the presence of high concentrations of the agent, data from this bioassay are not extensive enough to implicate oxygen sags as a factor in the toxicity.

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The TLMs for the two agents were estimated graphically (Figure C-6). In this case, the TLM is an integrated value approximating the concentration at which 50% of the experimental animals survived. The 96-hour TLM for PVA was 0.95%; the 48-hour TLM for PVA was 2.8%. Both the 48- and 96-hour TLMs for xanthan gum were 5.5%.

These TLM values, and particularly those for the high concentrations of the agents,* probably reflect the crab's response to conditions worse than would occur in the natural environment. Whereas the initial concentrations selected probably are realistic estimates of their potential strength in the natural environment, the chances of these concentrations persisting for 96 hours are extremely low. Tidal flushing of the beach and marsh shoreline would effectively dilute the agent concentrations. Thus, the 24-hour and 48-hour TLMs are more likely to reflect the worst-case conditions that the crabs would encounter. Similarly, the crabs in the natural environment could move out of and/or avoid any pockets of high agent concentrations. Additional testing with concentrations intermediate to those used in this test would more precisely define the TLMs for these agents, and would produce additional information on 24- and 48-hour toxicity.

The results of the bioassay apply only to the acute effects of these agents and do not provide any information about the effects of long-term, chronic exposure. The toxicity data generated also do not apply to any other marine organisms, or even to other Callinectes of different size, age, location, or physiological condition. Similarly, the data do not provide information about possible synergistic and antagonistic effects. Oil and oil/agent bioassays would provide valuable information in this regard.

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* Researchers observing the bioassay who had worked with the agents commented that the lowest PVA concentration (0.45%) was most similar in appearance (like skimmed milk) to the PVA/water mixture that occurred in the field during flushing. In contrast, the 5% PVA tank had a thick and milky appearance. Immediately after the introduction of the xanthan gum agent into the 10% tank, the water thickened to a consistency more like the agent than water.

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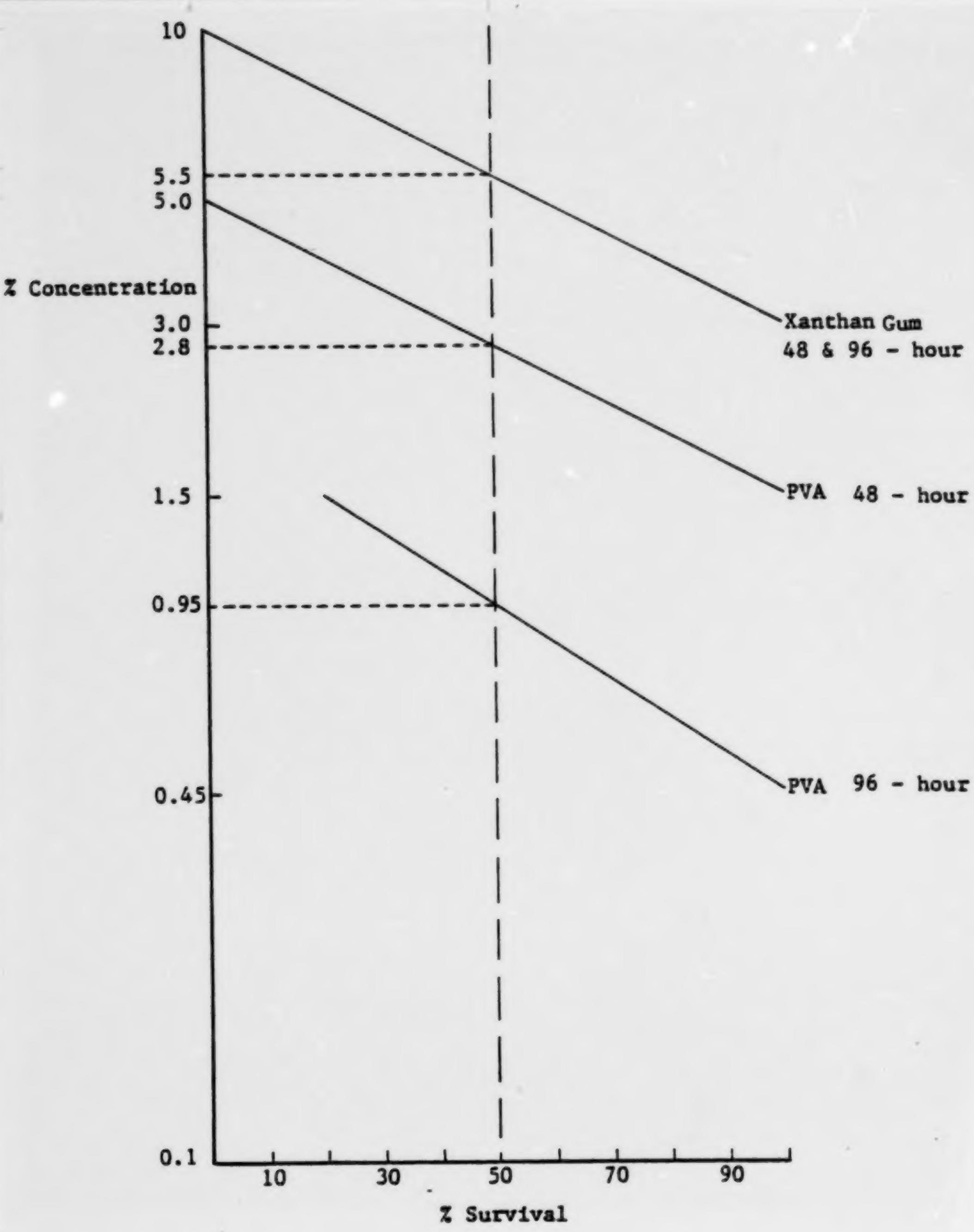

Figure C-6. Estimations of 50% tolerance limits by straight-line graphical interpolation.

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FINDINGS AND RECOMMENDATIONS

1. The acute static bioassay successfully established 96-hour toxicity ranges for the two agents: PVA (0.45% to 3%) and xanthan gum (3% to 10%).

2. PVA (as applied at 100%) is seemingly more toxic to first-stage juvenile *Callinectes* than is xanthan gum (as applied at 1%).

3. The PVA at 0.45% concentration did not have any apparent physiological effect on the crabs during the 96-hour test period.

4. The xanthan gum at 3% concentration did not have any apparent physiological effect on the crabs during the 96-hour test period.

5. The 96-hour TLM for PVA was 0.95%.

6. The 96-hour TLM for xanthan gum was 5.5%.

7. The PVA seemed to act like a weak acid. The persistent low pH level in the 5% tank could have contributed to the toxicity of the agent. Additional tests on the chemical behavior of PVA in water are recommended.

8. Acute bioassay tests with first-stage blue crab juveniles using five or six concentrations in the ranges delineated in (1) above should be performed. Additional testing with post-larval crabs, generally regarded to be more sensitive than first-stage juvenile, is also recommended.

9. Organism toxicity of oil and oil plus agents should be determined through additional bioassay work.

APPENDIX D

SURFACE TREATMENT AGENT TESTS - SIEDLER BEACH, NEW JERSEY, OCTOBER 18 AND 21, 1978

INTRODUCTION

Since 1976 Woodward-Clyde Consultants has been conducting a research program to evaluate the effectiveness of various natural and chemical agents in protecting shorelines from oil contamination. This program is jointly funded by research grants from the Environmental Protection Agency and the American Petroleum Institute.

As a continuation of this program, field tests of several surface protection agents were held at Seidler Beach, New Jersey, on October 18 and 21, 1978.

SCOPE

The field test program was originally planned to evaluate the effectiveness of the following four agents and a flowing film of water in protecting shorelines from oil contamination:

- Oil Herder, a surface collecting agent
- Corexit 7664, a dispersant
- BP 1100X, a dispersant
- Polyvinyl Alcohol/Borate-Gel, a film-forming chemical

Initially, the tests were to be conducted in the following manner. On four test areas the surface collecting agent, the BP 1100X dispersant, and Corexit 7664 undiluted were to be applied onto the water surface in front of an oil slick being carried on shore by winds and tides. On four other test areas the water spray, the polyvinyl alcohol/borate-gel, Corexit 7664 educted at 2% in water, and the surface collecting agent were to be applied to the shoreline substrate before an oil slick stranded on the shore.

Due to the wind conditions prevailing during the testing period, it was not possible to carry out the test program as originally planned. Onshore winds are necessary to move the test oil slicks toward the shoreline test areas. However, during the week-long test period, the winds blew offshore. These conditions necessitated a substantial revision of the original test plan.

In the revised test program the water spray system, the polyvinyl alcohol/borate-gel, and the educted Corexit 7664 were applied to the shoreline as planned. Based on recommendations of the manufacturers' representatives, Oil Herder and BP 1100X were not tested. Undiluted Corexit 7664 was sprayed on the shoreline test area rather than applied to the water surface. In the three tests conducted, oil was physically forced onshore with containment booms.

CONCLUSIONS

Based on the results of the October 1978 test program, the following conclusions are offered:

1. The flowing water film produced by the water spray system was most effective and provided the best protection from surface oil contamination and oil penetration into the substrate.

2. Polyvinyl alcohol/borate-gel did not reduce surface oil contamination. However, it did prevent oil from penetrating the substrate and appeared to facilitate removal of oil by flushing. As a surface barrier, the gel remained on the beach for only one tidal cycle.

3. The tests of Corexit 7664 as a protection agent were inconclusive. Visual observations indicated that although Corexit 7664 applied to the shoreline prior to oil contact did not reduce the initial amount of surface oil contamination, it appeared to facilitate the removal of oil. The use of Corexit 7664 did not reduce the bearing capacity of the test areas, i.e., make it quicksand.

RECOMMENDATIONS

Based on the findings of this study the following recommendations are offered:

- Additional field tests to evaluate Corexit 7664 and the other products (BP 1100X and Oil Herder) should be conducted when the oil is moved ashore by onshore winds and currents.

- In future testing a larger sediment sampling program will be needed to provide statistically significant samples.

- Sediment samples should be taken from the test plots for several days after a test to determine if the agents facilitate the natural cleaning of a shoreline by tidal action.

- For sand/gravel application, external flushing should be avoided. Any ensuing test program should be designed to evaluate several periods of natural tidal flushing.

- * The logistics and operational procedures for deploying and using a water spray system on a large scale should be investigated.

FIELD TESTS

Test Site

Field tests were conducted at Seidler Beach, located on the New Jersey coastline of Raritan Bay between Laurence Harbor and Cliftwood Beach (latitude 40° 27' 20", longitude 74° 14'). The beach is situated in the west corner of Raritan Bay, just southeast of the convergence of the Arthur Kill and Raritan River, and is bordered by the outfall of Marquis Creek to the northwest, a sewage treatment plant to the north, and Raritan Bay Beach to the southwest. Seidler Beach is approximately 1600 feet long and is owned by the Township of Old Bridge. The shoreline is primarily composed of coarse sand in the upper intertidal zone with large pebbles dominating the lower intertidal zone. Access to the beach is through an undeveloped 60-acre lot fronting Highway 35.

Test Oil

A light Iranian crude oil with similar characteristics to test oils previously used was selected as the representative oil for the testing of shoreline protection agents. Characteristics for this oil are given in Table D-1.

Controlled Spilling of Oil

Approximately 170 to 190 liters (45 to 50 gallons) of Iranian crude oil were spilled for each daily agent test. These volumes would provide a uniform oil loading of approximately 2 to 4 liters/ meter of shoreline, or about 50 to 75 liters of oil for each individual test area.

During each test the oil was spilled within the containment booms on a flooding tide just prior to high tide. The booms were then pulled up onto the beach, drawing the oil onto the test areas.

TABLE D-1. CHARACTERISTICS OF IRANIAN CRUDE

Characteristic	Value
Gravity	35.5 °API
Viscosity	
Kinematic	6.4 CS at 100°F
Pour Point	-20°F

Agent Evaluation Procedures

Three surface protection agents were evaluated during the test program. These were tested on the following days:

10/18/78	Polyvinyl Alcohol/ Borate Gel	Film-forming agent
	Water Spray	Flowing water film
10/21/78	Corexit 7664	Water-based dispersant

Film-Forming Agent and Water Spray

Two 25-meter-long test plots (one for the control and one for the PVA/borate-gel) and one 10-meter-long test plot (for the water spray) were laid out along the upper intertidal area at the southern end of Seidler Beach. Each test plot was separated by booms that were set in the beach sediments, extending into the water perpendicular to the beach (see Figure D-1).

The water spray system was constructed of a 10-meter section of 5-centimeter (2-inch) diameter PVC pipe with 1.27 centimeters (0.5 inch) flat fan jet spray nozzles fitted on 1.8-meter (6-foot) centers connected to a 378-liter/minute (100-gpm) centrifugal pump. The pump drew seawater from a suction line placed approximately 3 meters offshore. The spray pipe was placed on supports approximately 0.5 meter high along the upper intertidal area with the spray nozzles oriented to give a flat spray angled downward, toward the water. This orientation provided an even flowing film of water over the beach sediments.

The polyvinyl alcohol/borate-gel was applied in two parts using two separate spray systems over a 25- by 3-meter area in the upper intertidal zone. A premixed 5% solution of polyvinyl alcohol was sprayed across the test area using a gear pump and hose. Once the polyvinyl alcohol solution was applied, it was sprayed with a saturated borax solution, causing it to gel in place. Concentration and application rates of the film-forming chemicals used were:

	Concentration	Application
HV-Polyvinyl Alcohol	50 grams/liter	600 ml/m^2 (30 g/m^2)
Borax (sodium tetraborate decahydrate)	25 grams/liter	30 ml/m^2 (0.75 g/m^2)

Corexit 7664 - Dispersant

One 25-meter-long control plot and two 12.5-meter-long test plots were laid out long the upper intertidal area of the northern part of Seidler Beach (Figure D-2). One 12.5-meter test plot was sprayed with 5 liters of Corexit 7664 educted in a 2% solution through a fire hose. The other 12.5-meter test plot was sprayed with 5 liters of Corexit 7664 applied neat (undiluted) with a

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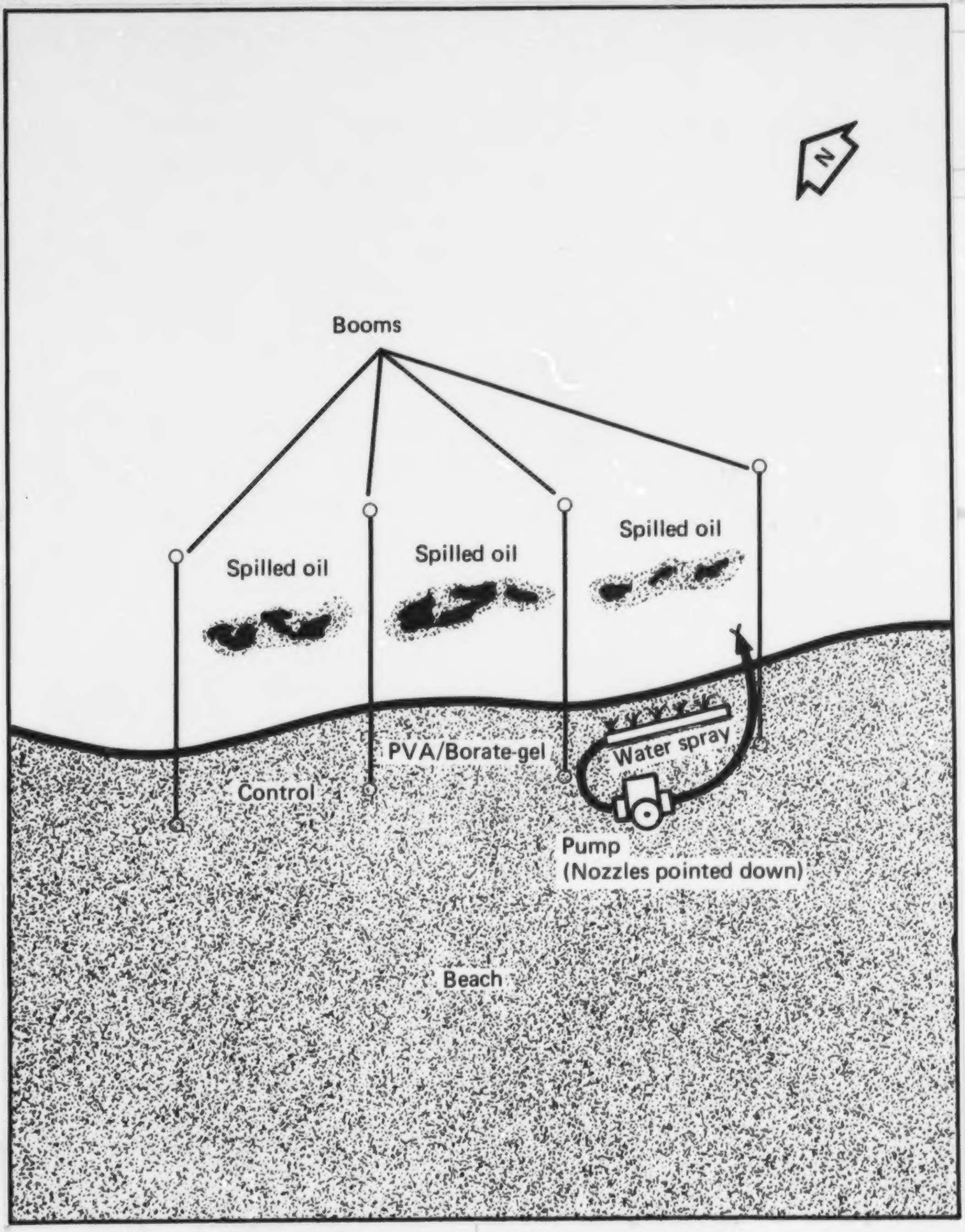
N
Booms
Spilled oil
Spilled oil
Spilled oil
Water spray
PVA/Borate-gel
Control
Pump
(Nozzles pointed down)
Beach

Figure D-1. Film-forming agent test configuration.

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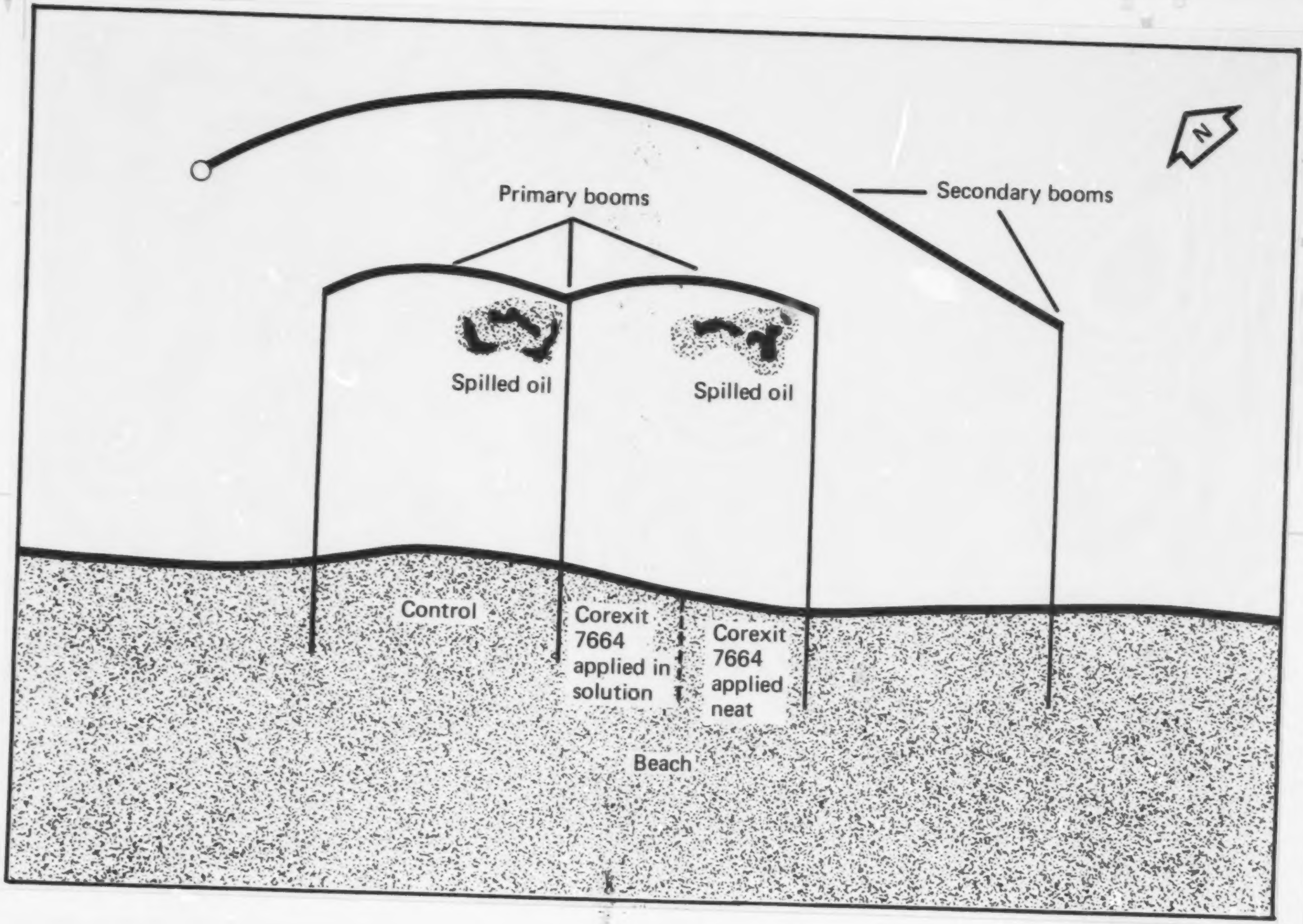
N
Primary booms
Secondary booms
Spilled oil
Spilled oil
Control
Corexit 7664 applied in solution
Corexit 7664 applied neat
Beach

Figure D-2. Dispersant test configuration.

backpack sprayer.

Test Procedure and Data Collection

All of the agent evaluation tests were conducted in a similar manner. The test procedure was:

1. Spill oil inside of booms for each test and control area.
2. Apply agent onto test areas.
3. Bring oil onto shoreline using containment booms, create waves on the shoreline using the wake of a small workboat driven parallel to the beach.
4. Approximately 45 minutes after oil is brought ashore, test and control areas are flushed with seawater using a fire hose and 100 gpm fire pump. (The water spray test area was not flushed after the shoreline was contaminated.) Flushing is conducted to determine if the agents prevent the oil from adhering to the sediment.

Table D-2 summarizes the test conditions and procedures. Data on the effectiveness of each surface protection agent was obtained visually and by taking sediment samples which were analyzed for oil content.

The sediment sampling program involved taking two surface samples and two subsurface samples (at a depth of 10 to 15 centimeters) in each test and control area, at two different times: (1) after oil came ashore, and (2) after each test and control plot was flushed (Figure D-3 shows sample locations). Samples were also taken in the lower intertidal area several hours after flushing when the receding tide had exposed the tide flats. Several background samples were taken on the test beach and on the control beach prior to the tests.

Cone pentrometer readings were taken on the dispersant test sites before and after the tests to determine if the use of dispersants on a shoreline altered the bearing strength (and the trafficability) of the beach.

A detailed description of the sediment sampling procedure is contained in Appendix D-1.

Biological Testing Program

A biological sampling and analysis program was conducted in conjunction with the dispersant tests. A description of this program and the results obtained is contained in Appendix D-2.

Test Results

General—

In all the tests, oil contamination of the substrate was very uneven. Because of the sporadic nature of the oil contamination the number of

TABLE D-2. SUMMARY OF TEST CONDITIONS - TEST AGENT

Test Condition	Polyvinyl Alcohol Borate 10/18/78	Control #1 10/18/78	Water Flush 10/18/78	Control #2 10/21/78	Corexit 7664 Neat 10/21/78	Corexit 7664 Educted 10/21/78
Time of agent application	Start 9:10 Stop 9:15	-	N/A	-	Start 11:17 Stop 11:25	11:26 11:31
Amount of agent used	2250 grams - PVA (45 liters - 5% soln) 50 grams - Borate	-	378 liters/ minute	-	5 liters	5 liters educted at 2%
Amount of oil spilled	57 liters	57 liters	57 liters	95 liters		95 liters for both plots
Time of oil spill	9:03 9:04	Start 9:00 Stop 9:01	9:06 9:07	Start 11:08 Stop 11:10		Start 11:14 Stop 11:16
Length and width of test area (meters)	25 x 3	25 x 5	10 x 3	25 x 5	12.5 x 5	12.5 x 5
Wind direction	--------------------	East	----------------	---------------	East	-----------------
Wind Speed	--------------------	0-10 mph	-----------------	---------------	0-13 mph	----------------

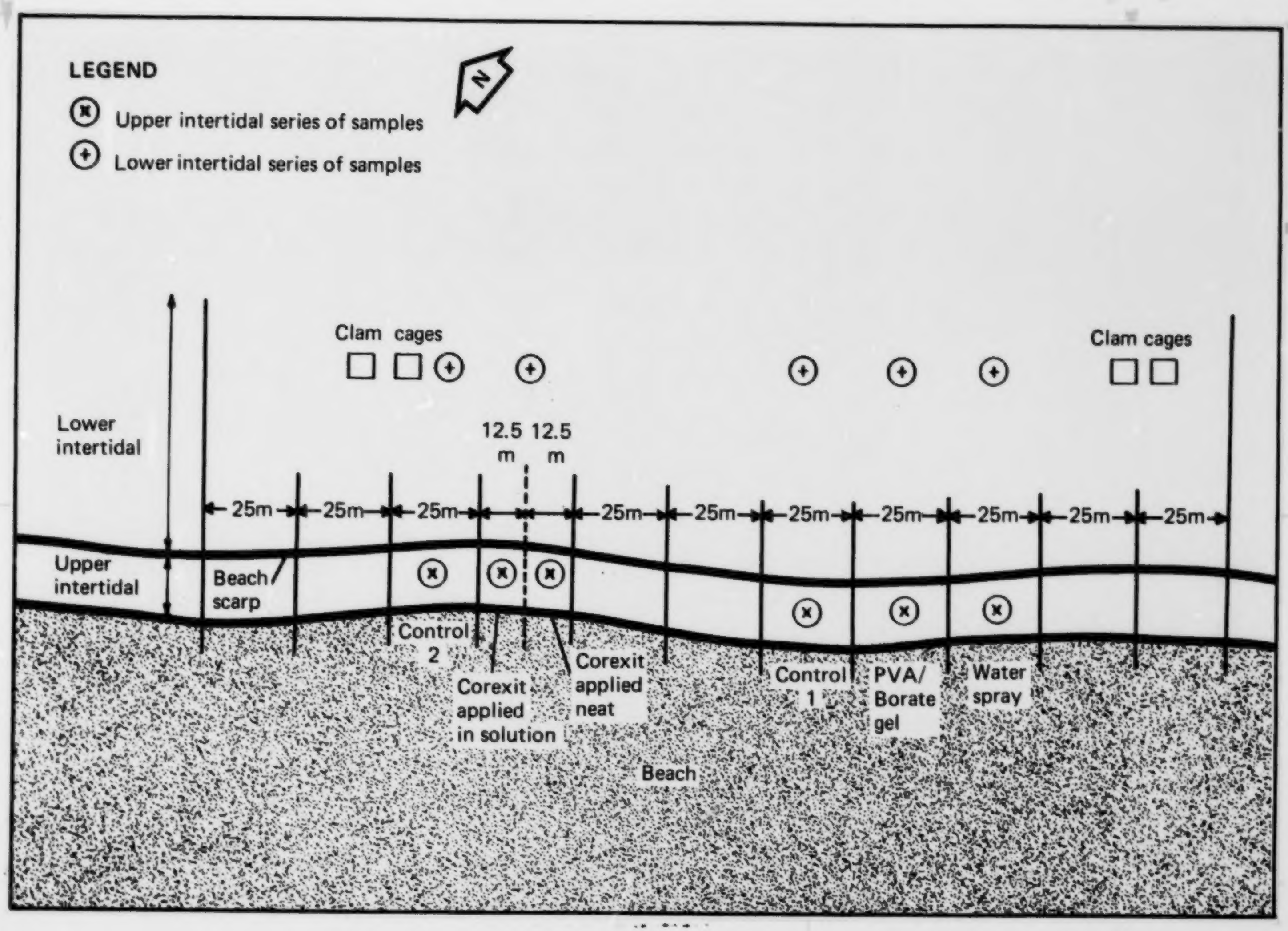
LEGEND
Upper intertidal series of samples
Lower intertidal series of samples
N
Clam cages
Clam cages
Lower intertidal
Upper intertidal
Beach scarp
12.5 m
12.5 m
25m
Control 2
Corexit applied in solution
Corexit applied neat
Control 1
PVA/ Borate gel
Water spray
Beach

Figure D-3. Sample location map.

substrate samples collected were insufficient to provide statistically significant results. In order to provide statistically significant data, the number of samples collected and analyzed would have had to have been increased by an order of magnitude which was beyond the funding limitations of the program. Therefore, care must be taken when interpreting or using the data presented in this report.

Although the test area appeared to be free of oil contamination prior to the tests, background (baseline) samples of the test beach and a control beach a mile away indicated background oil contamination levels in the substrate ranging from 8 to 39 mg/kg (ppm).

Polyvinyl Alcohol/Borate-Gel and Water Spray System--

The results of the polyvinyl alcohol/borate-gel and the water spray system are shown in Table D-3. The polyvinyl alcohol/borate-gel film did not prevent the substrate from becoming contaminated; however, it appeared to prevent oil from adhering to the shoreline sediment as both the visual observations and sediment sample results indicate. The film prevented oil from penetrating the substrate. A preliminary test application of the film suggested its persistence to be less than one or two tidal cycles. The water spray system proved to be quite effective, prevnting oil from contaminating the test zone by countercurrent flow of water over the beach.

Both the polyvinyl alcohoborate-gel and the water spray system appeared to prevent oil from penetrating the beach substrate. However, the beach is composed of firm sand and gravel and oil penetration of the control area was also minimal.

Corexit 7664--

The results of the educted and neat applications of Corexit 7664 are shown in Table D-4. The disparity in some of the replicate samples of one to two orders of magnitude make the results very difficult to interpret. Educting the same volume of dispersant onto the beach was faster and appeared to give more even coverage than applying the dispersant neat. Visual observations indicated that oil deposition on the dispersant-treated plots was only marginally less than on the control plot, with the least amount of oil present on the test plot where Corexit 7664 was educted in a 2% solution.

Visual observations of the test and control plots after they were flushed with seawater indicated that the dispersant-treated plots were more easily cleaned.

The sediment samples analyses indicate that there was more oil on the test and control plots after flushing than before flushing. This was not confirmed by visual observations and is an example of sampling error.

This use of dispersants did not appear to cause oil to deeply penetrate the sediments. The samples and visual observation taken at a depth of 10 centimeters indicate very little oil contamination of either the control plot or the dispersant-treated plots. However, after the test and control plots were flushed, a diffused sporadic band of oil was observed 3 to 5 centimeters below the surface in all three test plots, apparently related to the flushing operation.

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TABLE D-3. SAMPLE RESULTS AND VISUAL OBSERVATIONS OF POLYVINYL ALCOHOL/ BORATE-GEL AND WATER SPRAY AGENT TESTS

Test Series and Samples		Oil Contamination Before Flushing: Surface Sample Upper Intertidal mg/kg	Oil Contamination Before Flushing: Sample 10-15 cm Deep Intertidal mg/kg	Oil Contamination After Flushing: Surface Sample Upper Intertidal mg/kg	Oil Contamination After Flushing: Sample 10-15 cm Deep Upper Intertidal mg/kg	Oil Contamination of Lower Intertidal 24 Hrs After Test: Surface Sample mg/kg	Oil Contamination of Lower Intertidal 24 Hrs After Test: Sample 10-15 cm Deep mg/kg	Visual Observations and Comments
Control #1	#1	4050	50	2830	2	6	33	Before flushing - oil contamination was concentrated in a 0.5-cm band just beneath the surface.
	#2	3520	44	2680	39	8	7	After flushing - oil was more diffuse in a 1.25-cm band just below the surface.
Polyvinyl Alcohol Borate-Gel	#1	3880	0	45	6	20	0	Before flushing - test area appeared to be contaminated to some extent as control - oil in 0.3-cm band at surface.
	#2	433	0	141	7	17	5	After flushing - no visual oil remaining on area flushed.
Water Spray System	#1	9	0	Flushing not conducted on water spray test area		7	3	Only light oil sheen observed on test area - no heavy areas of oil concentration. Some erosion of beach surface caused by water spray.
	#2	5	3			8	20	

TABLE D-4. SAMPLE RESULTS AND VISUAL OBSERVATIONS OF COREXIT 7664 TEST

Test Series and Sample Numbers		Background Samples Before Tests		Oil Contamination on Test Area Before Flushing		Oil Contamination on Test Area After Flushing		Surface Sample Lower Intertidal Several Hours After Flushings mg/kg	Visual Observations and Comments
		Upper Intertidal mg/kg	Lower Intertidal mg/kg	Surface Sample mg/kg	Sample at 10-15 cm Depth mg/kg	Surface Sample mg/kg	Sample at 10-15 cm Depth mg/kg		
Control #2	#1	14	8	697	29	2990	79		Before flush - 1.5-cm band of oil contamination at surface diffusing downward.
	#2		39	64550	89	17290	83		After flush - some visible oil remained on beach sediments.
Corexit 7664 Educted at 2%	#1	12	12	48	15	11480	23	S-1 13	Before flush - occasional buried band of oil 0.75 cm thick. Some dispersed oil on water adjacent to test area.
								S-2 5	After flush - oil appeared to flush off beach fairly easily.
	#2	1		60	45	903	5	S-3 13	Some oil stain remained on substrate.
Corexit 7664 Applied Neat	#1	15		191	26	1180	-		Before flush - 1-cm band of oil contamination at surface. Test area received largest amount of oil contamination. Some dispersed oil on water adjacent to test area.
	#2			1140	64	1240	219		After flush - oil appeared to flush off beach. Some oil stain remained on sediments.

Bearing Strength Tests--

Cone pentrometer readings were taken of the control and dispersant test plots before and after the tests were conducted to determine if the use of dispersants would affect the bearing strength and trafficability of a beach. The results of the bearing strength survey are shown in Table D-5. As the table indicates, the use of dispersants did not change the bearing strength of the test areas.

Discussion

Water Spray System--

The countercurrent flowing water film produced by the spray system was the most effective of the three agents in protecting the shoreline from surface oil contamination, and preventing penetration of oil into the sediments. Some beach erosion did occur when the water spray impinging on the beach eroded a shallow trench approximately 15 centimeters wide by 2 to 3 centimeters deep along the length of the spray bar. Although the water spray system proved to be very effective, it might be difficult and expensive to implement on a large scale. At the flowrate tested, a pumping capacity of 11,340 liters/minute (3000 gpm) would be required for every 300 meters (1000 feet) of shoreline to protect. It is uncertain whether the high flowrate tested is required. Water spray systems could be used to protect smaller shoreline areas of high amenity or biologically significant value if the systems were already constructed and could be emplaced in a short time.

TABLE D-5. BEARING STRENGTH SURVEY OF TEST AREAS

Area	Averaged Cone Pentrometer* Readings Before Test	Averaged Cone Pentrometer Readings After Test
Control	72	75
Corexit 7664 Educted	74	75
Corexit 7664 Neat	74	83

* The cone pentrometer readings are a measure of the shearing resistance of the sediments, and can be directly related to the ability of earth-moving equipment to operate on the sediments without becoming immobilized. The range of pentrometer readings (72-83) from Siedler Beach indicate that rubber-tired earth-moving equipment could operate successfully on that particular beach.

Polyvinyl Alcohol/Borate-Gel--

The polyvinyl alcohol/borate-gel agent did not appreciably reduce surface oil contamination of the shoreline but did appear to prevent oil penetration into the substrate and to facilitate removal of oil by flushing. The persistence of the agent as an intact film was approximately one tidal cycle when applied to the upper intertidal area of a low-energy beach. Several hours to several days are required to formulate the polyvinyl alcohol solution, depending on how much agent is needed. The formulation requires that (5% by weight) dry polyvinyl alcohol powder be added to cold water, and stirred. The water is then heated to 93°C (200°F) and allowed to cool to room temperature. The resulting solution will remain stable for approximately 4 weeks. The time required for formulation and the short duration of persistence may severely limit the use of polyvinyl alcohol/borate-gel on a large scale.

Corexit 7664--

The Corexit 7664 tests were inconclusive in determining its effectiveness as a protection agent. Corexit 7664 appeared to reduce initial oil contamination of the beach surface somewhat, as indicated by the cloud of dispersed oil formed in the surf zone. No significant differences in the amount of oil initially dispersed as a function of near or diluted application was visually detectable.

Application of the agent using a hand sprayer was fairly time-consuming and would probably not be practical for actual use. Eduction using a fire hose provided a more acceptable rate of coverage.

The oil was removed by flushing with seawater. Flushing appears to be a factor in the success of the technique. When aimed directly at the oily sediment, some oil was removed, but some also appeared to be mixed more deeply into the sediments. Application of water just outside the edge of the oiled zone appeared to float the oil free without this mixing effect. Flushing far from the waterline (in dry sediment above the beach water table) was not successful. The dispersant did not reduce the bearing capacity or trafficability of the test areas where it was used.

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APPENDIX D-1

SEDIMENT SAMPLING PROCEDURES

1. During low tide on the day before each oil spill test, a single sediment sample is taken from the lower intertidal area of each test plot to be tested on the following day (with the exception of the test plots for CON1, PVAB, and WFA-B which are to be teted on the first day of the test).

2. Sample collection is carried out using a metal trowel. Sufficient sample volume is taken from the top 6 inches of the substrate to fill a 250-ml sample jar (each jar is prewashed with hexane and fitted with an aluminum foil inner seal to avoid contamination).

3. Once fitted, each jar is closed and frozen, using dry ice, and stored for analysis at a later date by the EPA.

4. Prior to the daily spill test, the above procedure is repeated for the upper intertidal area of each test plot to be tested that day. This sample and the above-mentioned lower intertidal sample are to be used as indicators of background hydrocarbon levels. Again, no background samples are taken for CON1, PVAB, and WFA-B, which are to be tested on the first day of the program.

5. Upon completion of the oil spill test, two sets of sediment samples (four samples in total) are taken in the upper intertidal area of each test plot. The two locations sampled are situated roughly 1 meter apart in the middle of the oiled test band in an area showing high oil contamination.

6. From each location, two different samples are taken: one surficial sample (0-2-inch interval) and one from a depth of 7 inches (5-7-inch interval). All four samples are collected and stored in the manner described previously.

7. Following the completion of the flushing portion of the test, this process is repeated with two surface and two subsurface samples taken in the upper intertidal portion of each test plot (no such sample is taken from WFA-B since it already involved flushing).

8. A final set of sediment samples (four samples in total) is taken in the lower intertidal area during the next low tide following the test. These samples are taken from the area adjacent to the clam cages (roughly 30 to 40 meters out from the base of the beach scarp). Again, two samples are taken from each location sampled, placed in sample jars, and frozen.

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NOTE: No post-test lower intertidal samples were taken for CON2, CORE, or CORN, since oil spilled in these test plots was prevented from reaching the lower intertidal area by booms and the prevailing winds.

9. In addition, two sediment samples are taken from the control beach: one prior to the onset of the test program and one following its completion. These samples are taken from the top 6 inches of substrate immediately adjacent to the clam cages. Two additional clam cage samples are also taken from the substrate adjacent to the two test beach clam cages following completion of the test program.

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APPENDIX D-2

LABORATORY INVESTIGATION OF IMPROVED MATERIALS FOR SHORELINE PROTECTION FROM OIL SPILLS

BACKGROUND AND APPROACH

The API/EPA has sponsored two series of investigations to identify materials that can be used to prevent contamination of shorelines in the event of an offshore oil spill. The first program initiated research into the mechanism of shoreline protection, devloped procedures to evaluate candidate materials, and recommended promising agents for use in protecting sandy and rocky shorelines and salt marsh areas threatened by oil. Three laboratories (Tracor, Exxon, and Shell) worked independently in this first program and evaluated polymeric film-forming materials, polysaccharide gels, microorganisms, inorganic coatings, and surface-active agents.

The second program was contracted to Woodward-Clyde Consultants with URS Research Company and Texas Research Institute, Inc. as subcontractors, with assigned tasks to compare to a common baseline reagents recommended by the first investigating laboratories, determine relative agent effectiveness, and conduct field tests of the more promising agents on salt marsh and sandy beach. A test site was located on Arthur Kill in Woodbridge, New Jersey, and tests were conducted during May 1977. The materials selected for field evaluation represented the protective mechanisms of a continuous polymeric film, a gelatinous organic coating, a low-concentration surfactant, and a flowing liquid barrier. The field-tested agents were:

1. Polyvinyl acrylate emulsion, AMSCO-REZ 3011 spray coated

2. 1% solution of xanthan gum spray coated

3. Oil Herder sprayed at the shoreline

4. Continuously flowing water

Of these, the polymer film and the polysaccharide gel showed good protective qualities but, more importantly, the tests indicated deficiencies in these materials which, if corrected, would greatly improve the overall performance. Application of the polymer emulsion to a sandy surface resulted in good coverage but on a rocky or uneven surface the coverage was not complete and resulted in coating gaps and subsequent oil penetration. This effect was not noted with the polysaccharide gel. In addition, the polymer film did not dry or set immediately on application, but when dry, persisted

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for several months. The xanthan gum solution did not require drying but lacked tenacity on the beach and was easily removed by wave action.

The objective for the current program was, therefore, to improve the applied materials' long- and short-term stability, setting characteristics, and application properties, without expending a large effort on new materials development. The approach taken was to rely heavily on the previous programs for guidance in selecting materials as well as test and evaluation methods.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The present study was directed to gelatinous materials, polymeric films with improved properties, and new classes of materials that could be applied as foam. The project was organized in three phases: identification of new materials, screening of these materials in the laboratory, and testing on simulated beaches. On the basis of previous EPA/API reports and recent literature, five new materials were selected for study: polyvinyl alcohols, modified polyvinyl acetate/acrylate, silicic acid gel, soluble starch, and a polyacrylamide gel. Gelling of polyvinyl alcohol with cross-linking agents to decrease its solubility and increase its mechanical strength was studied. These materials were screened in laboratory tests for ease of preparation and application, solubility in salt water, resistance to erosion, resistance to oil penetration and staining, foam-forming ability, and ability to form continuous coating. Those with potential for field application were subjected to testing in an oil spill on a beach simulator. Additionally, studies of the ultimate degradability of cross-linked polyvinyl alcohol were made and its manufacturers were queried for their best opinion of its ultimate breakdown behavior.

We have concluded from these studies that a high-molecular-weight, fully hydrolyzed polyvinyl alcohol, cross-linked with sodium borate, will serve as an effective agent to protect beaches from staining and penetration by an impinging offshore oil spill, is environmentally acceptable, and is free from drawbacks observed in the application of polyvinyl acetate emulsions and xanthan gum gels. Foamed polyvinyl alcohol performed best on a rocky, uneven beach; an unfoamed gel performed best on a flat, sandy beach. We also noted that the polyacrylamide emulsion, gelled with a cross-linking agent, had many desirable characteristics, but was flawed by the need for special procedures and equipment for its application.

Our recommendations are as follows:

Highest rank—recommended for field testing:

Cross-linked polyvinyl alcohol foams for rocky shorelines

Cross-linked polyvinyl alcohol gels for sandy beaches

Show promise but require special equipment development--not recommended for field tests:

Polyvinyl acrylamide gel

Soluble starch

Lowest rank—recommend dropping from further consideration:

Silicic acid gel

RESULTS AND DISCUSSION

Literature Review

A review of pertinent literature including previous API reports on shoreline protection, manufacturer's data, and other literature dealing with shoreline protection, oil spills, or hazardous chemical spills was made. A search of the NTIS data bank for related publications was also conducted. The literature review is listed in Appendix D-2-1.

Selection of Materials

Data from the previous beach protection program showed that a continuous polymeric film will prevent oil from penetrating into the beach and, also, that gelatinous materials similar to the xanthan gum solution could also act as a protective agent. More importantly, however, the previous field test pointed out several deficiencies in both of these materials. The polymer emulsion used as a continuous film-forming agent worked so well that it persisted on the beach through several months' exposure to the weather. Film formation, being dependent on the drying of the applied emulsion, was slow on a wet beach; in the event of rain it is assumed that film formation will not occur at all. On the other hand, xanthan gum, while not requiring drying, was not sufficiently durable on an open beach to provide protection. At the Sewaren test site, during the application of these two materials, xanthan gum gel was observed to form a more continuous coating on uneven, rocky sections of beach than the less viscous polyvinyl acrylate emulsion. In the present study the following characteristics were sought for a protective agent:

1. The ability to form a continuous polymeric film without the necessity of drying
2. The ability to form a film tough enough to withstand wave action, but that can be expected to degrade in a reasonable length of time
3. To have viscosity characteristics that will enable the material to flow over and fill gaps in rocky, uneven beach areas, as well as cover sand
4. To have sufficient tenacity for the beach to withstand wind and wave motion
5. To have short-term resistance to solubilization by salt water
6. To prevent penetration and staining by oil

7. Be relatively nontoxic and environmentally acceptable

Using these characteristics as a basis, five materials were initially selected:

1. Polyvinyl alcohol cross-linked with Congo Red
2. Polyvinyl alcohol cross-linked with sodium borate
3. Sodium silicate solution, neutralized to form a gel
4. A proprietary film agent manufactured by Whale Chemical Co.
5. Polyvinyl acrylate emulsion, as in the previous program but with the addition of a drying and/or degradation accelerating agent

The literature review resulted in the selection of two additional materials--soluble starch (a high-molecular-weight polysaccharide) and a low-molecular-weight polyacrylamide which can be cross-linked to form a sticky, gelatinous mass. Both of these satisfied the requirements of a protective agent and were tested in the laboratory. Materials, suppliers, and costs are summarized in Table D-6.

Gelling Polyvinyl Alcohol with Cross-Linking Agents

A separate study was made to determine applicable cross-linking agents to enhance gelation of polyvinyl alcohol solutions. Stable, as well as thermally reversible gels can be formed by reaction of polyvinyl alcohol with a number of reagents. Four cross-linking agents were investigated: Congo Red, sodium borate, boric acid, and gallic acid.

After cross-linking, polyvinyl alcohol becomes insoluble in water and increases in tensile strength. Thus, the advantage of cross-linking polyvinyl alcohol as applied to the beach is that the cross-linked material resists dissolution by impinging waves and maintains its mechanical integrity. Two methods were used to introduce the cross-linking agent into the solution. One was to mix a concentrated solution of the cross-linking agent directly into the polyvinyl alcohol solution. The second was to apply the polyvinyl alcohol to a beach substrate and to spray a cross-linking agent over the PVA. In the first instance, cross-linking agents blended directly into the polyvinyl alcohol solution resulted in an uncontrolled reaction. Small concentrations of cross-linking agents gel polyvinyl alcohol. As agitation and concentration of the cross-linking material increase, the solutions solidified into a rubbery mass. Overspraying polyvinyl alcohol solution with the cross-linking agent produced a gel with a tough surface film; polyvinyl alcohol foams became rubbery. Overspraying was the preferred method used for the remainder of the tests. The physical characteristics of the cross-linked PVA using each of the three agents varied and are shown in Table D-7. Briefly, gallic acid in concentrations up to 10% by weight of resin, slightly hardened polyvinyl alcohol films when oversprayed and only thickened a PVA solution. Congo Red, in concentrations of from 0.2% to 2% by weight of resin, coagulated the PVA into a gelatinous red mass in solution and produced a gelatinous surface when

TABLE D-6. MATERIALS SUMMARY

Material	Form (as Supplied)	Supplier	Cost ($/lb) $/kg	Cost as Applied ($/gal) $/liter	Cost ($/mile)*
Polyvinyl Alcohol Elvanol HV-L7D006	Powder	DuPont	(1.47) 3.24	(0.612) 0.162	1436
Polyvinyl Alcohol Elvanol 90-50 F	Powder	DuPont	(1.52) 3.35	(0.633) 0.167	1481
Polyvinyl Alcohol Geluatol 20-30	Powder	Monsanto	(0.875) 1.93	(0.364) 0.140	1242
Polyvinyl Alcohol Vinol 165	Powder	Air Products	(0.805) 1.78	(0.335) 0.089	789
Polyvinyl Alcohol Vinol 205	Powder	Air Products	(0.735) 1.62	(0.306) 0.081	718
Polyvinyl Alcohol Vinol 523	Powder	Air Products	(0.775) 1.71	(0.323) 0.085	754
Polyvinyl Acrylate Amsco-Res 3011	Liquid Emulsion 55% Solids	Union Oil	(0.32) 0.706	(2.930) 0.774	6865
Polyacrylamide XD-30123.01	Liquid	Dow Chemical	(0.30) 0.662	(1.250) 0.330	2927
Soluble Starch	Powder	Bon Ami Co.	(0.436) 0.961	(0.0728) 0.0192	170
Sodium Silicate	Powder	Baker Chemical	(0.475) 1.05	(0.187) 0.0494	438

* Beach area 1 mile long x 10 feet wide.

TABLE D-7. POLYVINYL ALCOHOL CROSS-LINKING AGENTS

Agent	PVA Conc.* (Wt. %)	Agent Conc. (% Resin)	Results
Congo Red	5	.2	Red gelatinous clots formed.
Congo Red	5	2	Thicker clots formed.
Boric Acid	5	Saturated Solution	Dripped into PVA with stirring--thickened and formed solid clumps.
Boric Acid	5	Saturated Solution	Misted over PVA--formed surface skin on contact--PVA thickened on standing
Borax	5	Saturated Solution	Dripped into PVA with stirring--thickened and formed solid clumps.
Borax	5	Saturated Solution	Misted over PVA--formed surface skin on contact--PVA thickened on standing.
Gallic Acid	5	10	Slow thickening of PVA solution.
Gallic Acid	5	10	Thin gelled skin formed when sprayed over PVA surface.

* Elvanol HU-L7D006.

oversprayed on a coated beach. The borates, sodium borate and boric acid, both produced very rapid coagulation of PVA in solution, and when oversprayed on a coated surface, immediately hardened the surface into a tough film. Because of the durability of the borate-treated polyvinyl alcohol, the relative low cost of the borates, the rapidity of the reaction and low toxicity, sodium borate was chosen as a cross-linking agent for use in the remainder of the tests.

Laboratory Screening

Samples of the materials enumerated on page 127, excepting the Whale Chemical Co. agent which was not available, were obtained for laboratory testing. Polyvinyl alcohols of low to high molecular weight and low to high degrees of hydrolysis were received. In general, molecular weight affects water solubility viscosity, and dry strength; degree of hydrolysis affects the alcohol's reactivity in cross-linking. While polyvinyl alcohol is only slightly soluble in cold water, the solubility limit is approximately 20% in hot water. Five percent solutions of six different polyvinyl alcohol formulations were prepared for laboratory screening. Gels of soluble starch, cross-linked polyacrylamide, and silicic acid were also prepared. Bench-scale procedures designed to test for the criteria set out on page 126 were performed. Detailed descriptions of these tests and preparation procedures are presented in D-2-2. Since little of the data gathered was of a quantitative nature, a scoring protocol of pluses or minuses was utilized. The better results are indicated by more pluses; negative attributes by minuses. The results of these tests are presented in Table D-8.

Simulated Beach Testing

The simulated beach system used to test agents in this program is essentially the same as that used on the previous API program. Three beaches with an area of 0.334 square meters each were attached to a mechanism that rocked the beaches through a 30-degree arc every 2 seconds. The beach surfaces were made of unwashed river sand and placed in the beach containers to a depth of approximately 3 inches. The agents to be tested were applied to one half of the beach surface; the untreated half served as a control. Agents were applied to beaches prewetted with 3.5% salt water. After drying, the appearance and texture of the coatings were noted. Approximately 2.0 liters of salt water were then added to the beaches and rocking was continued for 1 hour. Observations were then made of erosion, dissolution, or displacement of the coatings. Test oils, Kuwait crude and No. 2 fuel oil were added and the beaches again rocked for another hour. After the second hour, the water was drained from the beach, appearance was noted, and residual oil was washed from the beach surface with a stream of water. Observations again were made on the ability to remove the oil from the surface. Vertical sections of the beaches were then examined for oil penetration and staining. The results of these tests are given in Table D-9.

Additional Testing

It became apparent during the course of the laboratory phase of this program that materials not tested or combinations of materials not tested

TABLE D-8. LABORATORY SCREENING SUMMARY

		Preparation		Application		Foam Expansion				Erosion Resistance*		
Material	Form	Method	Rating	Method	Rating	% Initial	% at 17 Hrs	Rating	Coverability*	ml	Rating	Staining/ Cleanability
Elvanol HN-L7D006	Gel	Mix w/heat	+	Pour/spray	+	137	50	+	+	260	+	+
	Foam	Mix w/heat	+	Pour/spray	+							
Elvanol 90-50F	Gel	Mix w/heat	+	Pour/spray	+	175	25	+	-	200	+	+
	Foam	Mix w/heat	+	Pour/spray	+							
Vinol 105	Gel	Mix w/heat	+	Pour/spray	+	137	50	+	-	90	-	+
	Foam	Mix w/heat	+	Pour/spray	+							
Vinol 205	Gel	Mix w/heat	+	Pour/spray	+	312	Trace	+	-	180	+	+
	Foam	Mix w/heat	+	Pour/spray	+							
Vinol 523	Gel	Mix w/heat	+	Pour/spray	+	237	75	+	+	130	+	+
	Foam	Mix w/heat	+	Pour/spray	+							
Gelvatol 20-30	Gel	Mix w/heat	+	Pour/spray	+	337	0	+	-	100	+	+
	Foam	Mix w/heat	+	Pour/spray	+							
AMSCO-REZ 3011	Emulsion	As Rcvd.	+	Pour/spray	+	0		-	+	Did not erode	+	+
Soluble Starch	4% gel	Mix & heat	+	Pour hot, allow to cool	-	0		-	+	50	-	-
Sodium Silicate	Gel	Mix & Acidify	-	Pour	+	0		-	-	5	-	-
Polyacryl-amide	Gel	Crosslink w/reagents	-	Premix and rapidly pour	-	0		-	N/A	N/A	N/A	N/A

* Polyvinyl alcohol cross-linked with borax
+ - Acceptable
- - Unacceptable

TABLE D-9. SIMULATED BEACH SUMMARY

Material	Application	Erosion	Kuwait	#2 Oil	Overall
Elvanol HV-L7D006	Gel not cross-linked	-	N/A	N/A	- (rapid erosion)
	Gel/Borax	+	+	+	+
	Foam/Borax	+	+	+	+ (edges tended to lift from sand)
Elvanol 90-50F	Gel/Borax	+	+	+	+
	Foam/Borax	-	+	+	- (low strength)
Vinol 105	Gel/Borax	-	+	+	- (low strength)
	Foam/Borax	-	+	+	- (low strength)
Vinol 205	Gel/Borax	+	+	+	+
	Foam/Borax	-	+	+	- (low strength)
Vinol 523	Gel/Borax	+	+	+	+
	Foam/Borax	+	+	+	+
Gelatol 20-30	Gel/Borax	-	+	+	- (low strength)
	Foam/Borax	-	+	+	- (low strength)
AMCO-REZ 3011	Emulsion	+	+	+	- (long drying time required)
Sodium Silicate	Gel	-	-	-	- (very short persistence)

showed promise for use in shoreline protection. Included in these materials is a mixture of polyvinyl alcohol and silicate gel, a mixture of water-soluble starch and polyvinyl alcohol, and other polyelectrolytes similar to the polyacrylamide. Brief laboratory observations were made but a detailed investigation of these materials could not be made within the scope of the program. These observations are given in Table D-10.

None of the procedures outlined under laboratory screening and beach simulation testing address the ultimate degradability of coating materials. This was determined, in the Sewaren field tests, to be a defect of the polyvinyl acetate/acrylate coatings. To gain insight into this process two mini-tests were conducted. First, test patches of sand were prepared and coated with polyvinyl alcohol solution, polyvinyl alcohol foam, both of these cross-linked with sodium borate, and polyvinyl acetate/acrylate emulsion. These patches were allowed to dry thoroughly. Sections were cut from the test plots, immersed in salt water, and allowed to soak. Intermittent observations showed the uncross-linked polyvinyl alochol to hydrate to a mucilaginous film that could be broken or separated between the fingers after a day or two, and the acetate/acrylate copolymer film to lose little of its initial strength or toughness after 3 weeks.

TABLE D-10. MIXTURES AND OTHER MATERIALS

1. 5% Polyvinyl alcohol, uncross-linked - 1% Silicic Acid Gel

   Can be foamed. Foam stabilized by silicic acid gel.

   Drying time increased.

   Dried foam discontinuous and crumbly.

2. 28% Polyvinylacetate/acrylate - 2% Soluble Starch

   Dries to a hard, tough film.

   Film softens only slightly during one-week exposure to salt water.

3. Polyacrylamide Gel

   Forms dense gel that cannot be poured.

   Dries very slowly, but rehydrates to its original form.

   High resistance to erosion by salt water.

To study the breakdown of dried film of these materials, these films were prepared by dipping circular loops of stainless steel wire. Dried samples were exposed to bright sunshine all day for one week while controls were stored in a dark cabinet. Daily observations during this period showed no change in the color, texture, or brittleness of the exposed samples. At the end of a week's exposure infrared transmittance spectra of the film showed no evidence of ultrviolet-induced chemical decomposition. On the eighth day of exposure the outdoor samples were inadvertently briefly subjected to brief morning mist, after which they were brought inside to dry. On drying, all of the polyvinyl alcohol films shrunk and curled--the polyvinyl acetate/acrylate films were unaffected. We feel the capacity of the polyvinyl alcohol films to readily hydrate and their tendency to shrink and curl on drying will cause mechanical degradation of applied film in a reasonably short period in the moist environment of the beach.

EQUIPMENT REQUIRED FOR ON-SITE APPLICATION

The solutions recommended for field test of this program can all be pumped through standard centrifugal or positive-displacement pumps. However, for application of foam, special pumping systems must be used. Several varieties of foam-generating equipment are commercially available for application of foam to fires, application of insecticides, and for other purposes where expanded solutions are required. In general, foam generators work by injecting air into a stream of the fluid being pumped and dispensing the fluid/air mixture through a sized screen to control the resulting foam bubbles. For the purpose of field testing, a limited amount of foamed material could be generated by using a commercial foam pump, or by foaming in a container, such as a 55-gallon drum fitted with a high-speed mixer. The resulting foam could then be poured on the surface to be coated. Application of cross-linking agents required for polyvinyl alcohol can be accomplished through use of hand-held garden-type sprayers.

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APPENDIX D-2-1

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APPENDIX D-2-2

PREPARATION OF MATERIALS AND SCREENING TESTS

PREPARATION

Polyvinylalcohol Solutions

Polyvinylalcohols (5% by weight), granular or powder, was added to cold water with stirring to form a slurry. The slurry was heated under continuous stirring until all turbidity disappeared. This occurred at 65°-70°C. No significant increase in viscosity was noted in solution of this concentration on cooling.

Polyvinylacrylate (AMSCO RES-3011)

No preparation necessary. Apply as received.

Soluble Starch

Soluble starch (4% by weight) was added to cold water with stirring to form a suspension. The suspension was heated with stirring until no further decrease in turbidity could be noticed. This occurred near 100°C. Upon cooling, the solution formed a viscous gel.

Silicic Acid Gel

A solution of sodium meta-silicate (1%, based on SiO_2 content) was prepared in cold water. The pH of this solution was adjusted to 8.5 by dropwise addition of concentrated HCl with stirring. The solution was then allowed to stand. A dense mucilaginous driable gel formed within 15 minutes.

Polyacrylamide (Dow XD-30123.01)

Two solutions were prepared:

1. 0.75 ml of 40% glyoxal was added to 100 g of polyacrylamide emulsion.
2. 1.5 g of Na_3PO_4 $12H_2O$ in 100 g of H_2O.

The two solutions were poured together and rapidly stirred. A tenacious gel formed with 2 to 3 minutes.

FOAMABILITY/FOAM STABILITY

Two hundred ml of each agent were placed in a Waring blender and stirred at high speed for 60 seconds. The volume of the resulting foam was measured in a graduated vessel and the time required for the foam to collapse was observed.

RESISTANCE TO STAINING AND OIL PENETRATION

Test objects (a wooden stick, a glass microscope slide, a patch of glass fixer cloth) were coated with the protective agent. The objects were allowed to dry, dipped briefly into a solution of salt water, then dipped into a vessel of crude oil. The tenacity of the oil was observed. The object was then rinsed with a stream of water and again examined for oil staining or penetration.

COVERING ABILITY AND EROSION RESISTANCE

Twenty-cm squares of screen wire were dipped in preparations of each protective agent and withdrawn. The squares were then allowed to dry. Completeness of coverage was noted. A 3.5% salt solution (simulating sea water) was allowed to drip onto each material at a rate of 60 to 70 drops/minute from a height of 30 cm. The volume of solution required to break through the coating was recorded.

APPENDIX D-2-3

DETAILED PREPARATION PROCEDURES, RECOMMENDED AGENTS

The recommended agent is high-molecular-weight, fully hydrolized polyvinyl alcohol (DuPont Elvanol HV or equivalent). This material is available as a powder in 50-lb bags.

The PVA is prepared as a 5% by weight solution (0.44 lb PVA per gallon H_2O in fresh water) using the following procedure:

1. Add the weighted powder to a known volume of fresh, cold water while mixing. A 55-gallon drum can be used with an electric drum-type mixer.

2. Heat the mixture while stirring to approximately 200°F to dissolve the PVA. The solution will become clear when the powder dissolves. Two or three external band heaters, Chromalox PFD-130 SG (120 volt, 1500 watt) or equivalent, should be used along with a minimum of 2 inches of external fiberglass insulation.

3. Allow the solution to cool with the container covered to prevent evaporation. The solution can be stored for 4 to 6 weeks before use if desired.

PVA application to the beach is at the rate of 1/2 gallon/m^2.

The borate solution is made using sodium tetraborate decahydrate dissolved in water at the rate of 30 gm/liter (.25 lb/gal). This is ordinary borax available at a grocery store. Stir or shake the mixture until completely dissolved.

Apply the borax solution over the PVA on sand or gravel in a fine spray at the minimum rate of 30 ml/m^2 (1/8 oz/m^2). Excess borax will not decrease the effectiveness of the PVA coating.

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APPPENDIX D-2-4

RECOMMENDED AGENT TOXICITY

POLYVINYL ALCOHOL

Polyvinyl alcohol is generally considered nontoxic. It is approved by the FDA for food contact applications and is widely used in contact with skin as a textile sizing. PVA is not listed in the NIOSH Registry of Toxic Materials.

In water, PVA has been reported (Long-Term Biochemical Oxygen Demand of Elvanol Polyvinyl Alcohol, E. I. DuPont de Nemours & Co., 1970) to have a BOD (% by weight oxygen consumed) of 1% at 5 days and 3% at 30 days. PVA would therefore have little, if any, effect on aquatic life.

BORAX

Data has been presented (R. W. Sprague, The Ecological Significance of Boron, U. S. Borax Research Corporation, Anaheim, California, 1972) indicating the toxicity of borax as follows:

LD_{50} (rats): 4.5 - 6.1 gm/kg

Minimum lethal dose (minnows): 1.9% in H_2O

Boron compounds can affect plant growth. Tolerant crops can be grown in soils containing up to 3.75 ppm boron (32 ppm as borax). Sea water contains an average concentration of 4.6 ppm boron. The amount of borax recommended for beach applications (900 mg/m^2), when dispersed in sea water, is not expected to adversely affect marine plant growth.

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